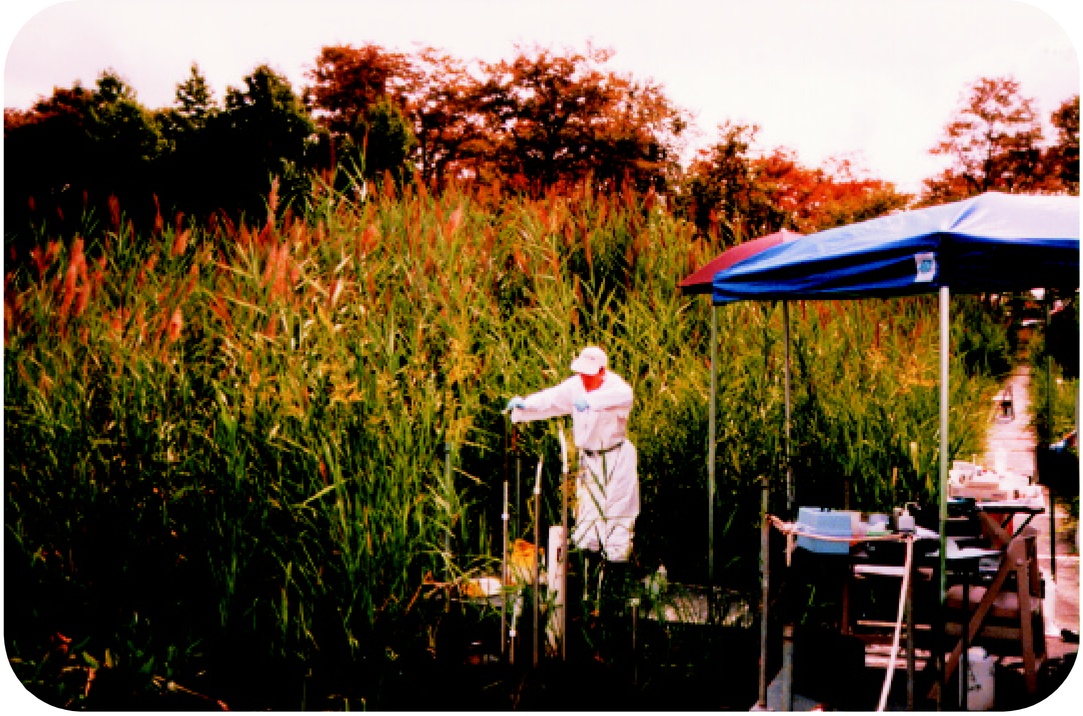
NATURAL ATTENUATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN A FRESHWATER TIDAL WETLAND, ABERDEEN PROVING GROUND, MARYLAND

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 97-4171



Prepared in cooperation with the

U.S. ARMY GARRISON, ABERDEEN PROVING GROUND
ENVIRONMENTAL CONSERVATION AND RESTORATION DIVISION
ABERDEEN PROVING GROUND, MARYLAND

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

Cover: Collection of ground-water samples from small diameter piezometers in wetland study area, West Branch Canal Creek, Aberdeen Proving Ground, Maryland.

(Photograph by Michelle M. Lorah, U.S. Geological Survey)

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Baltimore, Maryland

1997

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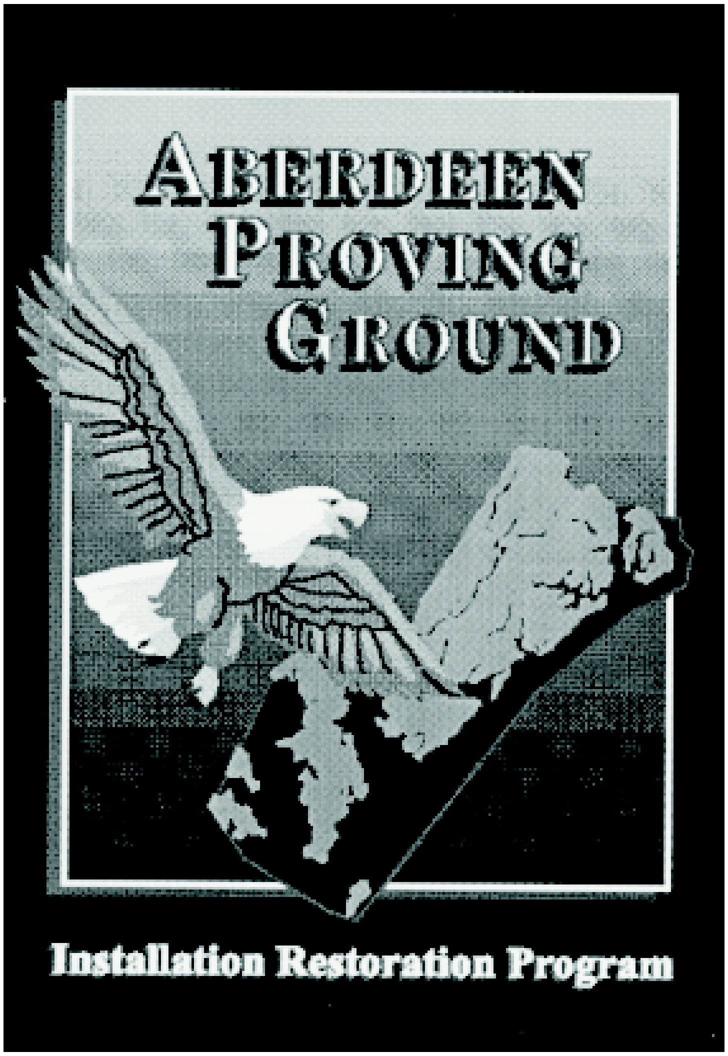

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1997

Aberdeen Proving Ground, Edgewood Area

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FIGURES

FIGURES--Continued

FIGURES--Continued

FIGURES--Continued

TABLES

TABLES--Continued

CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	2.54	centimeter
inch (in.)	25,400	micrometer
inch per year (in/yr)	0.02540	meter per year
foot (ft)	0.3048	meter
foot per day (ft/d)	0.3048	meter per day
foot per year (ft/yr)	0.3048	meter per year
foot squared per day (ft^2/d)	0.09290	meter squared per day
mile (mi)	1.609	kilometer

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Other abbreviated units of measure: Water temperature, chemical concentration, and other chemical and physical properties of constituents are given in metric units. Water temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$^{o}F = 1.8\,(^{o}C) + 32$$

Chemical concentration in water is expressed in milligrams per liter (mg/L), micrograms per liter (µg/L), millimoles per liter (mmol/L), or micromoles per liter (µmol/L). Chemical concentration in soil is expressed as micrograms per kilogram of dry soil (µg/kg), and ratios of aqueous concentrations to concentrations in soil are expressed as liters per kilogram (L/kg).

Molecular weight and other mass expressions are expressed in grams (g), and density is given in grams per cubic centimeter (g/cm^3). Other abbreviations used include milliliter (mL) or liter (L) for volume measurements, and micrometer (µm) or nanometer (nm), which equals 1 x 10^{-6} and 1 x 10^{-9} meter, respectively, for length.

NATURAL ATTENUATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN A FRESHWATER TIDAL WETLAND, ABERDEEN PROVING GROUND, MARYLAND

By Michelle M. Lorah, Lisa D. Olsen, Barrett L. Smith, Mark A. Johnson, *and* William B. Fleck

ABSTRACT

Ground-water contaminant plumes that are flowing toward or currently discharging to wetland areas present unique remediation problems because of the hydrologic connections between ground water and surface water and the sensitive habitats in wetlands. Because wetlands typically have a large diversity of microorganisms and redox conditions that could enhance biodegradation, they are ideal environments for natural attenuation of organic contaminants, which is a treatment method that would leave the ecosystem largely undisturbed and be cost effective. During 1992-97, the U.S. Geological Survey investigated the natural attenuation of chlorinated volatile organic compounds (VOC's) in a contaminant plume that discharges from a sand aquifer to a freshwater tidal wetland along the West Branch Canal Creek at Aberdeen Proving Ground, Maryland. Characterization of the hydrogeology and geochemistry along flowpaths in the wetland area and determination of the occurrence and rates of biodegradation and sorption show that natural attenuation could be a feasible remediation method for the contaminant plume that extends along the West Branch Canal Creek.

The aquifer, which received contaminants in the past from sources that were located upgradient of the current eastern boundary of the wetland, is about 40 to 45 feet thick in the study area. The overlying wetland sediments consist of two distinct layers that have a combined thickness of about 6 to 12 feet--an upper unit of peat and a lower unit of silty to sandy clay or clayey sand. Head distributions show strong vertical gradients, and flow directions are predominantly upward through the wetland sediments. Tidal fluctuations, however, cause some reversals in ground-water-flow directions and changes in discharge locations, which affect the distribution and transport of contaminants. The average linear velocity of ground water is estimated to be about 2 to 3 feet per year along vertical flow lines in the wetland area, and the total ground-water discharge along a 1-foot-wide strip of the wetland extending from the eastern wetland boundary to the creek is in the range of 0.13 to 0.25 feet squared per day.

The major parent contaminants in the aquifer were trichloroethylene (TCE); 1,1,2,2-tetrachloroethane (PCA); carbon tetrachloride (CT); and chloroform (CF). The aquifer was typically aerobic, but ground water in the wetland sediments

became increasingly anaerobic along the upward flow direction. Iron-reducing conditions were predominant in the lower wetland sediment unit composed of clayey sand and silt, and methanogenesis was predominant in an upper unit composed of peat. Total concentrations of VOC's and the relative proportions of parent compounds to anaerobic daughter products changed substantially as the contaminants were transported upward through these changing redox environments. Concentrations of the parent compounds TCE and PCA ranged from about 100 to 2,000 micrograms per liter in the aquifer beneath the wetland, whereas concentrations of daughter products were low or undetectable. In contrast, the parent compounds commonly were not detected in ground water in the wetland sediments, but the daughter compounds 1,2-dichloro-ethylene (12DCE), vinyl chloride (VC), 1,1,2-trichloroethane (112TCA), and 1,2-dichloroethane (12DCA) were observed. 12DCE and VC were the dominant daughter products in the wetland sediments, even where PCA was the primary parent contaminant discharging to the wetland. The presence of these daughter products in water in the wetland sediments indicates that TCE and PCA are degraded by reductive dechlorination reactions in the naturally anaerobic wetland sediments.

Although production of daughter products was observed, total concentrations of the VOC's decreased upward through the 6- to 12-feet-thick wetland sediments and were less than 5 micrograms per liter near the surface. The daughter products are apparently further degraded by these anaerobic processes to non-chlorinated, non-toxic endproducts, or are removed by other attenuation processes such as aerobic degradation or volatilization.

Several sets of anaerobic microcosms, some amended with TCE concentrations of 400 or 990 micrograms per liter (3.0 or 7.5 micromoles per liter) and one amended with PCA concentration of 480 micrograms per liter (2.9 micromoles per liter), were constructed in the laboratory using wetland sediment and ground water from the study area. These microcosm experiments confirmed field observations that 12DCE and VC are the dominant daughter products from anaerobic biodegradation of both TCE and PCA. Production of 112TCA and 12DCA also was observed in the PCA-amended microcosms, but concentrations were lower than those of 12DCE and VC. These results indicate that degradation of PCA occurs through both hydrogenolysis and dichloroelimination pathways under anaerobic conditions. Daughter products were not observed in sterile controls, except for relatively low concentrations of 12DCE in the PCA-amended controls, suggesting that the reactions were predominantly microbially mediated. Parent and daughter concentrations in the microcosms decreased to less than 5 micrograms per liter in less than 34 days under methanogenic conditions, thus showing extremely rapid biodegradation rates in these organic-rich wetland sediments.

Maximum potential rate constants for biodegradation of TCE and PCA, which were calculated from the microcosm experiments assuming first-order degradation rates, ranged from 0.10 to 0.31 per day under methanogenic conditions, corresponding to half-lives of 2 to 7 days. The rate constant for TCE biodegradation under sulfate-reducing conditions was 0.045

per day (half-life of 15 days), which is lower than under methanogenic conditions. These estimated rate constants for the wetland sediments are two to three orders of magnitude higher than those reported in the literature for TCE biodegradation in microcosms constructed with sandy aquifer sediments.

Aerobic biodegradation rates for *cis*-12DCE, *trans*-12DCE, and VC were in the same range as those measured for TCE and PCA under anaerobic conditions in microcosm experiments. Thus, production of these daughter products by anaerobic biodegradation of TCE and PCA could be balanced by their consumption where oxygen is available in the wetland sediment, such as near roots and land surface. In the aerobic microcosm experiments, biodegradation of *cis*-12DCE, *trans*-12DCE, and VC occurred only if methane consumption occurred, indicating that methanotrophs were involved in the process. Aerobic biodegradation was fastest for vinyl chloride and slowest for TCE in the microcosm experiments. These results agree with other laboratory and field studies that have shown faster degradation by methane-utilizing cultures when the compounds are less halogenated.

Equilibrium sorption isotherms were measured in 24-hour batch tests and used to estimate distribution coefficients (K_d's) to describe the ratios of sorbed to aqueous concentrations of PCA and the daughter products *cis*-12DCE, *trans*-12DCE, and VC. The estimated K_d's for PCA, *cis*-12DCE, *trans*-12DCE, and VC were about 2.3, 1.8, 2.4, and 1.3 liters per kilogram of sediment, respectively. Sorbed concentrations of PCA, *cis*-12DCE, and *trans*-12DCE in the wetland sediments, therefore, would be expected to be about twice the concentration measured in the water, whereas sorbed concentrations of VC would not be much greater than the aqueous concentrations. Coefficients of retardation, which were calculated using the K_d's and an advective flow velocity of about 2 feet per year, indicate that sorption alone would cause the movement of the contaminants in the wetland sediments to be 6 to 10 times slower than the advective ground-water flow.

Biodegradation and sorption, therefore, are significant natural attenuation mechanisms for chlorinated hydrocarbons in these wetland sediments. The relatively thin layers of wetland sediments are critical in reducing contaminant concentrations and toxicity of the ground water before it discharges to the wetland surface and the creek, and natural attenuation in the wetland sediments could be an effective remediation method for the ground-water contaminants.

INTRODUCTION

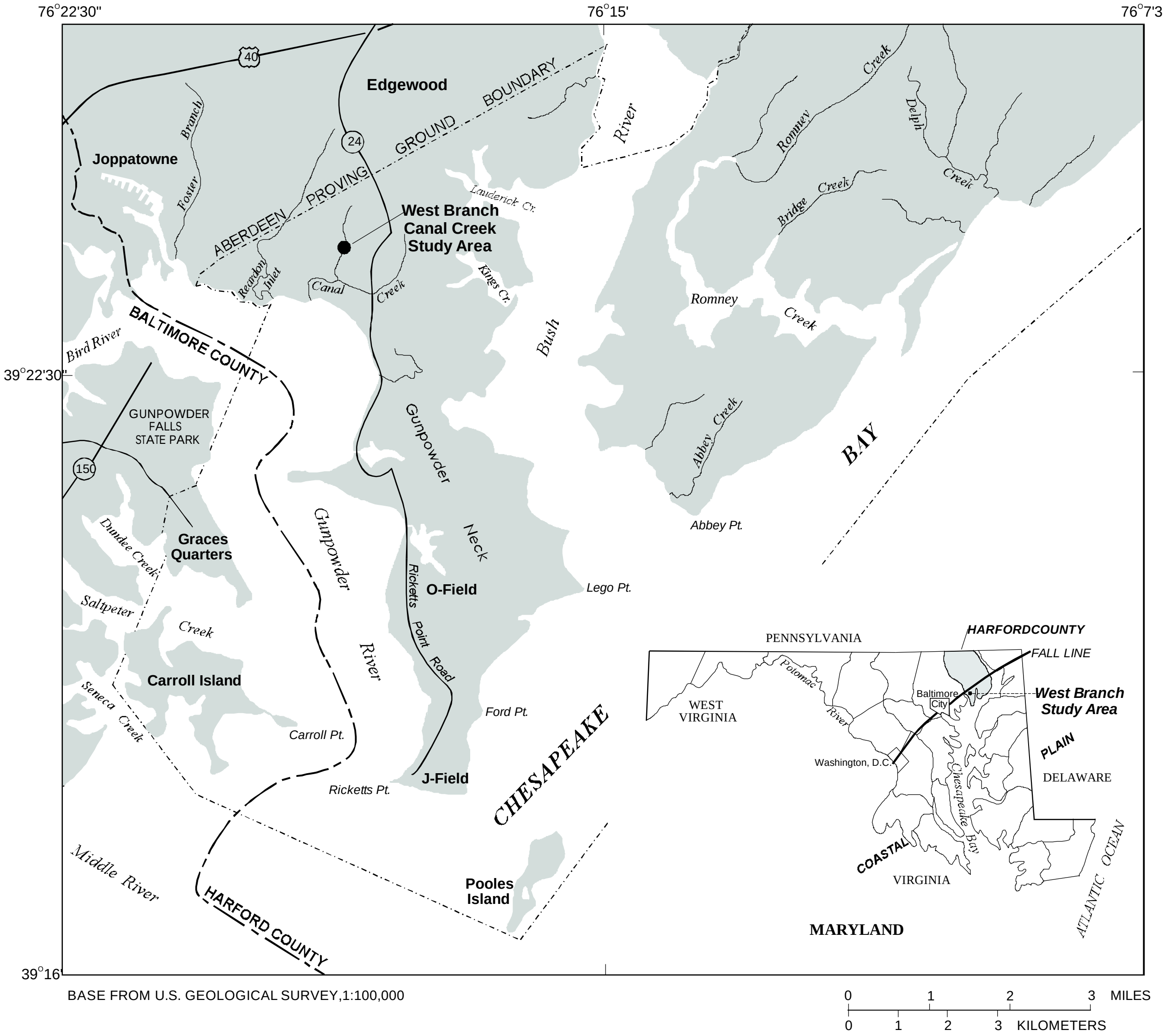
A large number of military installations are located near surface-water bodies where wetlands are a dominant part of the landscape. Ground-water contaminant plumes that are flowing toward or currently discharging to wetland areas present unique remediation problems because of the hydrologic connections between ground water and surface water and the sensitive habitats in wetlands. Available engineered clean-up methods would seriously impact the viability of these ecosystems. For example, some remediation methods such as pump-and-treat could dewater the wetland and destroy the ecosystem. Pump-and-treat remediation could also be highly inefficient and prohibitively expensive because of the potential to pump surface water along with contaminated ground water and of the potential for hydrophobic organic contaminants to sorb to organic-rich wetland sediments. Natural attenuation, however, is a promising *in-situ* remediation method for ground-water contaminants that would keep the ecosystem largely undisturbed and be cost effective.

The Canal Creek area of Aberdeen Proving Ground (APG), a U.S. Army base in Maryland (fig.1), has been used to develop, test, and manufacture military-related chemicals since World War I. Most of the manufacturing and experimental plants were located between the two branches of Canal Creek, a tidal creek. An investigation conducted by the U.S. Geological Survey (USGS) during 1985-92 showed that a large plume of contaminated ground water was present in a shallow sand aquifer along the West Branch Canal Creek and that the contaminated ground water was probably discharging to the creek and its surrounding freshwater wetlands (Lorah and Clark, 1996) (fig. 2). Chlorinated volatile organic compounds (VOC's) that are common industrial solvents, including trichloroethylene and 1,1,2,2-tetrachloroethane, were the major ground-water contaminants present upgradient from the wetlands. Hydrologic and ground-water-quality data, however, were not collected in the wetlands as part of that or any other previous study at APG.

An understanding of the hydrology and the distribution and fate of contaminants in the wetlands is needed to evaluate feasible ground-water remediation methods for the plume extending along the West Branch Canal Creek. In 1990, APG was placed on the National Priorities List established under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), and the U.S. Army and U.S. Environmental Protection Agency (USEPA) Region III signed an Interagency Agreement for investigation and remediation of the Canal Creek area and other areas at APG. The USGS, under a contract with the U.S. Army Environmental Conservation and Restoration Division at APG, began a study in October 1992 to determine the distribution, fate, and movement of the volatile organic contaminants in a selected area of the wetlands along West Branch Canal Creek. Partial funding was obtained under SERDP (Strategic Environmental Research and Development Program), a multi-agency effort that supports environmental research, development, demonstration, and applications programs. The purpose of this study is to determine if natural attenuation of the chlorinated VOC's occurs as the ground water flows through the wetland sediments. Natural attenuation can then be evaluated by APG as a possible remediation method for the contaminant plume along West Branch Canal Creek.

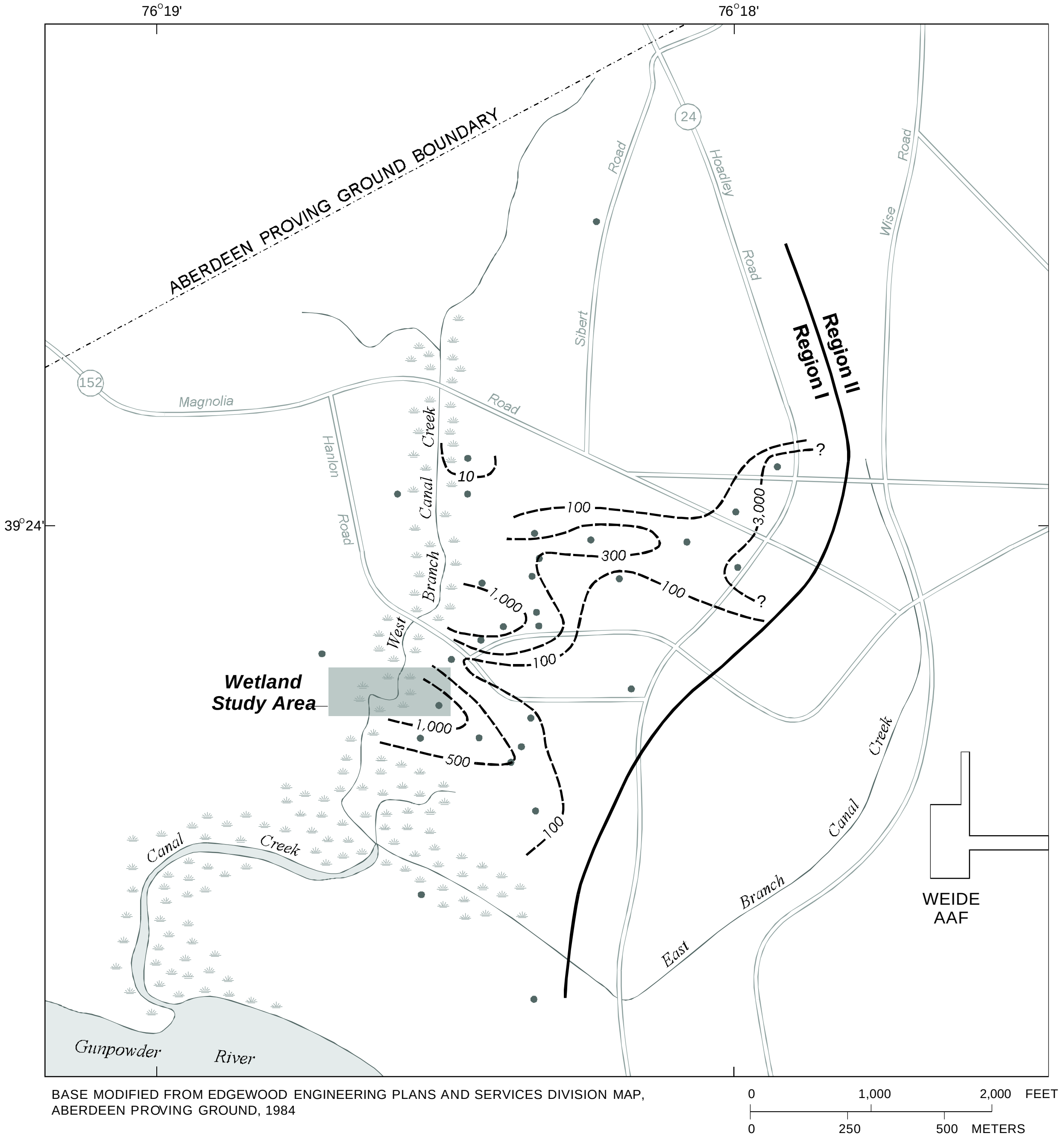
"Natural attenuation" is a general term for any combination of natural processes that act to reduce contaminant concentrations, mobility, or toxicity. Possible natural attenuation processes include biodegradation, abiotic degradation, volatilization, sorption, and dispersion (Wiedemeier and others, 1996, p. 1-1). Biodegradation is commonly the primary destructive process for organic ground-water contaminants, because abiotic chemical reactions occur at a slower rate than biologically mediated reactions for most contaminants. Sorption and volatilization are nondestructive processes that reduce dissolved concentrations by transferring the contaminants to another media (sediment and air, respectively). Dispersion, which consists of molecular diffusion and mechanical mixing, results in a decrease in contaminant concentrations but not in a net loss of contaminant mass.

Natural attenuation may be considered a feasible ground-water remediation method if migration of significant levels of contaminants to sensitive receptors is prevented. Evaluation of the potential for natural attenuation as a remediation method at a site requires detailed hydrogeological, chemical, and biological characterization to determine whether contaminants are being attenuated; an assessment of risks to public health and environmental receptors; and long-term monitoring to ensure protection of public health and the environment (Rifai and others, 1995; Wiedemeier and others, 1996). The primary receptors along the West Branch Canal Creek are the terrestrial and aquatic biota. A toxicity assessment was conducted in the wetland study



BASE FROM U.S. GEOLOGICAL SURVEY,1:100,000

Figure 1. Location of Canal Creek area and West Branch study area, Aberdeen Proving Ground, Maryland.



BASE MODIFIED FROM EDGEWOOD ENGINEERING PLANS AND SERVICES DIVISION MAP, ABERDEEN PROVING GROUND, 1984

EXPLANATION

?– –10– –	APPROXIMATE LINE OF EQUAL TOTAL ORGANIC HALOGEN CONCENTRATION -- Interval, in micrograms per liter, is variable. Queried where uncertain. Sampled in July-September 1988.
▬▬	BOUNDARY BETWEEN REGION I AND REGION II
●	WELL SITE

Figure 2. Location of the wetland study area along the West Branch Canal Creek, Aberdeen Proving Ground, Maryland, and the distribution of total organic halogen in the Canal Creek aquifer upgradient from the wetland (modified from Lorah and Clark, 1996, p.106).

area by the U.S. Army Center for Environmental Health Research (USACEHR) (formerly the U.S. Army Biomedical Research and Development Laboratory) and the University of Maryland and will not be discussed in this report.

The objectives of the USGS study were to (1) define major ground-water flowpaths and hydrologic interactions between the aquifer, wetland, and surface water; (2) determine the distribution of contaminants along ground-water flowpaths; (3) determine the major geochemical and microbial processes affecting the volatile organic contaminants; and (4) evaluate the effect and significance of other natural attenuation processes, including sorption and volatilization, on the fate and mobility of the volatile organic contaminants in the wetland. The study focused on extensive characterization of the processes occurring along two major ground-water flowpaths in a relatively small area of the wetland (fig. 2). Biodegradation processes were investigated most thoroughly because of their importance as the primary destructive process for organic contaminants. Information gained through this study on the natural attenuation processes should be transferable to similar wetland areas at APG and elsewhere.

Purpose and Scope

The purpose of this report is to describe the natural attenuation of chlorinated VOC's in the wetland study area along the West Branch Canal Creek. Characterization of the hydrogeology is presented first, providing the framework needed to understand the distribution and movement of contaminants and to quantify the extent of natural attenuation. The distributions of volatile organic contaminants and redox-sensitive constituents are examined along two major ground-water flowpaths to provide evidence for the occurrence of natural attenuation and to evaluate geochemical factors controlling the possible natural attenuation processes. Natural attenuation processes that are evaluated include biodegradation and sorption, with emphasis on biodegradation. The potential for dispersion and dilution of the contaminants is discussed as part of the characterization of the hydrogeology and contaminant distribution. Volatilization experiments are ongoing at the site and are not presented in this report.

To determine the hydrogeology and the distribution and fate of contaminants in the wetland area, sediment cores and ground-water samples were collected primarily along two transects (fig. 3). Hydrogeologic sections were constructed from lithologic and mineralogical data. Head distributions and estimates of hydraulic conductivity are used to determine ground-water-flow directions and velocities and to estimate the total discharge to the wetland and creek. During June-October 1995, ground-water samples were collected from 87 piezometers, which are screened at discrete intervals in the wetland and aquifer sediments, to obtain the overall distribution of VOC's and redox-sensitive constituents. Samples were then collected from 28 to 30 selected piezometers during March-April, June, and August 1996 to characterize seasonal effects on concentrations. In addition, porous-membrane sampling devices, commonly called "peepers," were used to obtain water samples over 1-in.-intervals in the shallow wetland sediment. The distributions of VOC's and redox-sensitive constituents are primarily discussed here, but all water-quality data are reported in Olsen and others (1997).

Biodegradation processes were evaluated using field evidence of the occurrence of parent and daughter compounds and of the distribution of redox-sensitive constituents and other geochemical parameters. Laboratory microcosm experiments were conducted under anaerobic and aerobic conditions to elucidate and confirm field evidence of biodegradation processes. Microcosm experiments were done to study the degradation of two of the major ground-water contaminants--trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA). Equilibrium sorption constants were estimated from batch laboratory experiments. Selected sediment samples collected from the wetland also were analyzed for VOC's to determine sorbed concentrations.

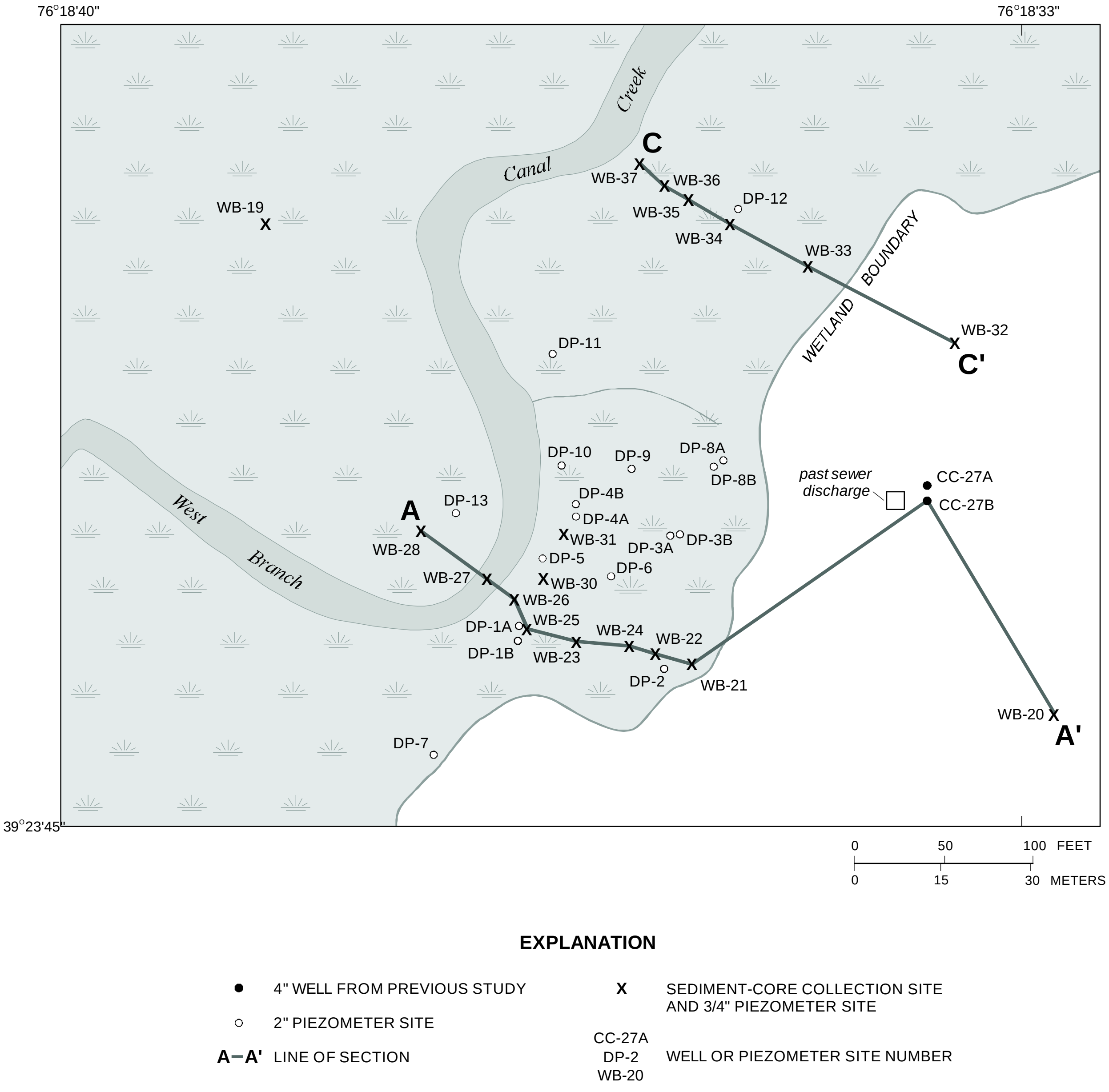


Figure 3. Locations of sampling sites and sections A-A' and C-C' in the wetland study area along the West Branch Canal Creek.

Description of Study Area

Geographic Setting

The study area is located in the Canal Creek area of APG, near the head of the Chesapeake Bay in the Coastal Plain Physiographic Province of Maryland (fig. 1). Canal Creek, the creek for which the study area is named, flows southward from the confluence of its East and West Branches into the Gunpowder River, an estuary located at the southwestern edge of the study area (figs. 1 and 2). The creeks and estuaries in the study area are tidally influenced, and the tidal amplitude ranges from about 0.5 to 2.0 ft. Freshwater wetlands, classified as "estuarine, emergent, irregularly flooded wetlands" (Durda and others, 1991, p. 7-66), surround much of the West Branch Canal Creek and the reach of Canal Creek below the confluence of its two branches. Wetland areas were more extensive in the past; however, landfilling operations eliminated many wetland areas, especially along the East Branch Canal Creek.

The vegetation is typical of tidal freshwater marshes in the Mid-Atlantic region (Marilyn Garcia, ICF Kaiser Engineers, Abingdon, Md., written commun., 1994). Along the eastern bank of the study area, the vegetation consists largely of a monotypic stand of common reed (*Phragmites australis*), except near piezometer site DP-12 (fig. 3) where there is a zone containing cattail, pickerelweed, and southern wild rice. Vegetation near the piezometers on the western bank consists of three zones--one dominated by common reed, one by southern wild rice, and one by narrow-leaf cattail. Vegetation in the wetland area does not show overt signs of stress, except within the streambed where vegetative cover is minimal (Marilyn Garcia, written commun., 1994).

Hydrogeologic Setting

The regional geology of the Canal Creek area is characterized by thick, wedge-shaped deposits of unconsolidated Coastal Plain sediments that dip southeastward (fig. 4). The Canal Creek aquifer, which ranges from 30 to 70 ft thick in the Canal Creek area, is the primary contaminated aquifer (Lorah and Clark, 1996). The lower confined aquifer, which underlies the approximately 60-ft-thick lower confining unit (fig. 4), is not known to be contaminated (Lorah and Vroblesky, 1989; Lorah and Clark, 1996). The upper confining unit, Canal Creek aquifer, lower confining unit, and lower confined aquifer are composed of sediments of the Cretaceous Potomac Group (Oliveros and Vroblesky, 1989, p. 11).

Two distinct hydrogeologic regions, Region I and Region II (figs. 2 and 4), were delineated in the Canal Creek aquifer in a previous study (Lorah and Clark, 1996, p. 55). The present wetland study area along the West Branch Canal Creek is in Region I. In Region I, the Canal Creek aquifer is unconfined or semiconfined where the overlying upper confining unit crops out (fig. 4). The shallow ground-water flowpaths in Region I are short, and most recharge and discharge is local. The general direction of flow in the aquifer is toward the West Branch Canal Creek from both sides of the creek, and there is a southwestward component of flow toward the East Branch Canal Creek near its junction with the West Branch (fig. 2). Deep flow in the aquifer also can enter the regional flow system and flow downdip to the southeast. Recharge occurs upgradient from the wetlands on both sides of the creek and is primarily from rainfall infiltration. Discharge from the aquifer in Region I occurs through wetland sediments, streambanks, and bottom sediments along the West Branch Canal Creek and a small portion of the lower East Branch Canal Creek. In Region II, most of the aquifer is confined, except for an area where the upper confining unit was eroded by a Pleistocene paleochannel, and most ground water flows in the deep, regional system.

Site History

Since 1917, APG has been the primary chemical-warfare research and development center for the United States. Most of APG's plants for chemical manufacturing and munitions filling were concentrated in the area between the West and East Branches of Canal Creek (fig. 2). The chemicals produced included chlorine, mustard gas, tear gas, phosgene, clothing impregnating material, white phosphorus,

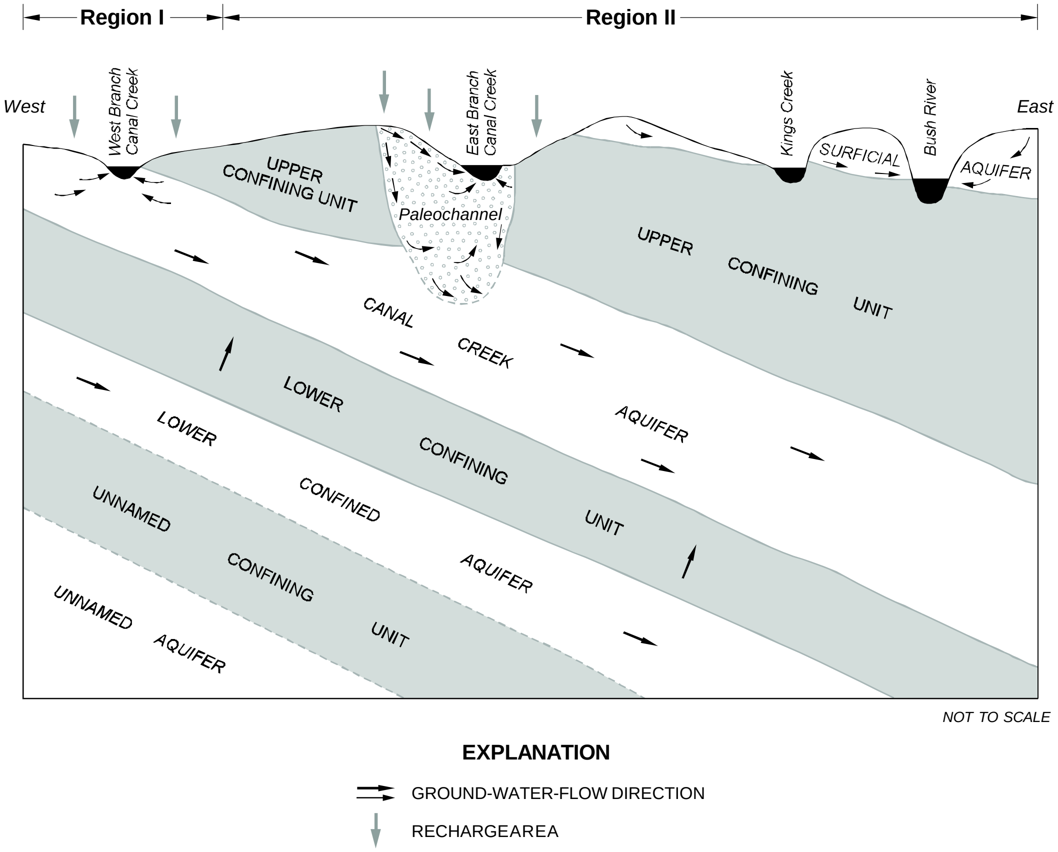


Figure 4. Generalized hydrogeologic section showing directions of ground-water flow in the Canal Creek area (modified from Lorah and Clark, 1996, p.11).

pyrotechnics, and arsenicals. After World War II, large-scale production and filling operations declined sharply, and many of the plants have since been demolished or abandoned. Historical activities in the Canal Creek area are detailed in Nemeth (1989) and are summarized in Lorah and Clark (1996, p. 20).

Chlorinated organic solvents, which were used as raw materials, decontaminating agents, and degreasers, were common waste products from the manufacturing and filling plants and from other miscellaneous activities in the study area (Lorah and Vroblesky, 1989; Lorah and Clark, 1996). The primary method of waste disposal from the manufacturing and filling plants until the late 1970's was by discharge to sewers that led to the East and West Branches of Canal Creek. Leaks through the sewerlines, which were constructed of vitrified clay during World War I, were probably a common problem. Release of waste products to the environment by spills, landfilling, and discharge to sewers resulted in ground-water contamination, including the plume along the West Branch Canal Creek (Lorah and Clark, 1996) (fig. 2). Trichloroethylene (TCE), 1,1,2,2-tetrachloroethane (PCA), carbon tetrachloride (CT), and chloroform (CF) were the four major contaminants present in ground water in the Canal Creek area that were known to have direct sources from use and disposal (Lorah and Clark, 1996, p. 117).

Before and during World War II, wastes generally received little or no treatment prior to discharge. Wastes that could not be put through the sewer systems were often dumped or buried in the wetland areas along Canal Creek. Some of the old sewerlines discharged into areas that are now covered with fill material, including one discharge point that was located in the wetland study area (fig. 3). Chemical wastes, including tars, sludges, and empty chemical containers may have been placed in landfill areas, although fill material in the study area appeared to consist predominantly of construction debris and pieces of old buildings. Construction and building material was pushed into the wetland study area during demolition of a chlorine plant in the late 1960's. None of the known contaminant sources that could have contributed to ground-water contamination near the wetland study area have been active in two or more decades. Continued dissolution of residual DNAPL's (dense non-aqueous-phase liquids) in the aquifer, however, is a likely current source of contamination (Lorah and Clark, 1996, p. 169).

Acknowledgments

The authors thank the following people and agencies for their important contributions to this study. John Wrobel of the U.S. Army Environmental Conservation and Restoration Division, Aberdeen Proving Ground, coordinated many aspects of the project. The U.S. Army Corps of Engineers installed the piezometers and assisted in collection of sediment-core samples. A crew from Aberdeen Technical Center, supervised by Pete Pritchard, provided technical support that included building walkways and a bridge through the wetland area. Thanks also is given to Henry Gardner, Thomas Shedd, and Alan Rosencrance of USACEHR, Fort Detrick, Maryland, for providing the analytical chemistry trailer and support associated with its operation.

The authors also are grateful to colleagues that assisted in collection of hydrogeologic and water-quality data during this study--Peggy Nemoff, Elizabeth Marchand, and Colleen Donnelly, all of the USGS in Baltimore, and Allison O'Brien, Christopher Jacobs, Michael Johnson, Paul Harvey, and Gerald Garcia of the U.S. Army Environmental Conservation and Restoration Division, Aberdeen Proving Ground. Denise Coutlakis, formerly of the USGS in Baltimore and currently with the USEPA in Washington, D.C., participated in monitoring network installation and data collection in the reconnaissance phase of the project. Frederick Tenbus of the USGS in Baltimore also assisted in some hydrogeologic interpretations. In addition, Edward Miller provided valuable support in the analytical chemistry trailer as a volunteer with the USGS. Discussions with Dr. Joel Baker, Dr. Karen Prestegaard, and Dr. Douglas Capone at the University of Maryland were helpful on various aspects of the project design.

BACKGROUND ON NATURAL ATTENUATION PROCESSES

The widespread occurrence of ground water contaminated with VOC's has led to numerous field and laboratory investigations to determine the fate and behavior of these compounds in the environment. "Natural attenuation" is a relatively recent term that has been used to refer to all the natural processes that control the fate of contaminants in the environment, including biodegradation, sorption, volatilization, and dispersion, and to recognize that these processes could act to naturally contain or remediate contaminated ground water (Wiedemeier and others, 1996, p. 1-1). Other terms that are virtually equivalent to "natural attenuation" include "intrinsic remediation" or "passive remediation." "Intrinsic" or "*in situ* bioremediation" are other terms that have been used because biodegradation is often the predominant mechanism in the subsurface that alters or destroys contaminants. Natural attenuation is gaining recognition as an alternative remediation technology that can be cost-effective and equally protective of health and the environment as conventional "active" systems, such as pump-and-treat remediation (National Research Council, 1993; Lovelace and Feldman, 1996). The USEPA recognizes natural attenuation as a potential remedial approach under the Superfund, RCRA (Resource Conservation and Recovery Act Corrective Action), and UST (Underground Storage Tank) remediation programs and is currently preparing a directive clarifying their policy on the use of natural attenuation (U.S. Environmental Protection Agency, 1988, 1990; Lovelace and Feldman, 1996).

Natural attenuation is not really a new technology because it has been well developed as a means of remediation for easily degraded petroleum products. The use of natural attenuation for remediation of chlorinated solvents, however, is less well developed (National Research Council, 1993, p. 3), although knowledge of the fate of these compounds in ground water has increased greatly since the early 1980's. Background on the major processes that could naturally attenuate chlorinated VOC's is given here, focusing on the primary source contaminants that were known to be present near the wetland area (Lorah and Clark, 1996)--TCE, PCA, CT, and CF. A conceptual model of natural attenuation at the West Branch wetland area is then presented.

Microbial and Abiotic Degradation

In general, biologically-mediated degradation reactions involve electron transfer, and the preferred degradation pathway for a given compound in the subsurface is dependent on the oxidation state of the organic compound and on the local ground-water chemistry and microbial populations. Microorganisms gain energy for growth and reproduction by catalyzing oxidation-reduction reactions, which require an electron donor and an electron acceptor. Organic contaminants can be degraded by serving as either an electron donor that becomes oxidized or as an electron acceptor that becomes reduced. Microorganisms, however, do not always gain energy from degradation of contaminants; instead, degradation may be an incidental reaction, commonly referred to as "secondary utilization" or "cometabolism", where the presence of primary substrates to support microbial metabolism is required (National Research Council, 1993, p. 17-22). Abiotic degradation generally occurs at much slower rates than microbially mediated reactions (Vogel, 1994). For a few compounds, however, abiotic degradation can be a significant process in ground-water systems where flow rates are low.

Anaerobic Degradation

Because the carbon atoms in highly chlorinated VOC's, including TCE, PCA, CT, and CF, have a relatively high oxidation state, they are microbially degraded most easily through reduction reactions (rather than through oxidation reactions) under anaerobic conditions. Under anaerobic conditions, chlorinated VOC's can be biodegraded by a type of reductive dehalogenation reaction called hydrogenolysis, which entails the sequential replacement of chlorine atoms by hydrogen to produce more reduced, less-chlorinated products (Vogel and others, 1987; Bouwer, 1992). In general, the rate of hydrogenolysis decreases as the degree of chlorination of the aliphatic hydrocarbon decreases. During hydrogenolysis, the chlorinated VOC's are utilized by microorganisms as an electron acceptor to support respiration. Other natural or anthropogenic compounds that are suitable electron donors (substrates) must be present for this reductive dehalogenation to occur. Possible electron donors are hydrogen, low-molecular weight organic compounds (lactate, acetate, methanol, or glucose), and fuel-related compounds that are easily oxidized (benzene, toluene, and ethylbenzene).

During the first step in hydrogenolysis of TCE, dichloroethylene (DCE) compounds are produced (fig. 5). Of the three possible DCE isomers, several studies have indicated that the *cis* isomer of 1,2-dichloroethylene (*cis*-12DCE) predominates over *trans*-12DCE and that 1,1-DCE is the least significant intermediate (Bouwer, 1994). The DCE compounds can then be reduced to vinyl chloride (VC), which can be further reduced to ethylene (Freedman and Gossett, 1989; Beeman and others, 1994) and ethane (de Bruin and others, 1992). Ethylene and ethane are desirable nontoxic end products, whereas the daughter products DCE and VC are just as, or more, toxic than TCE. The desirable end products could be difficult to achieve in most subsurface environments because of a lack of sufficient natural organic matter to provide electron donors (Chapelle, 1993, p. 370).

Laboratory experiments have shown that hydrogenolysis can occur under iron-, nitrate-, and sulfate-reducing conditions and methanogenic conditions (Freedman and Gossett, 1989; Bagley and Gossett, 1990; Bouwer, 1994). The rates of hydrogenolysis of highly chlorinated VOC's, however, tend to be greatest under the highly reducing conditions associated with methanogenesis than under less reducing conditions (McCarty and Semprini, 1994). Although a sulfate-reducing enrichment culture was capable of dechlorinating tetrachloroethylene

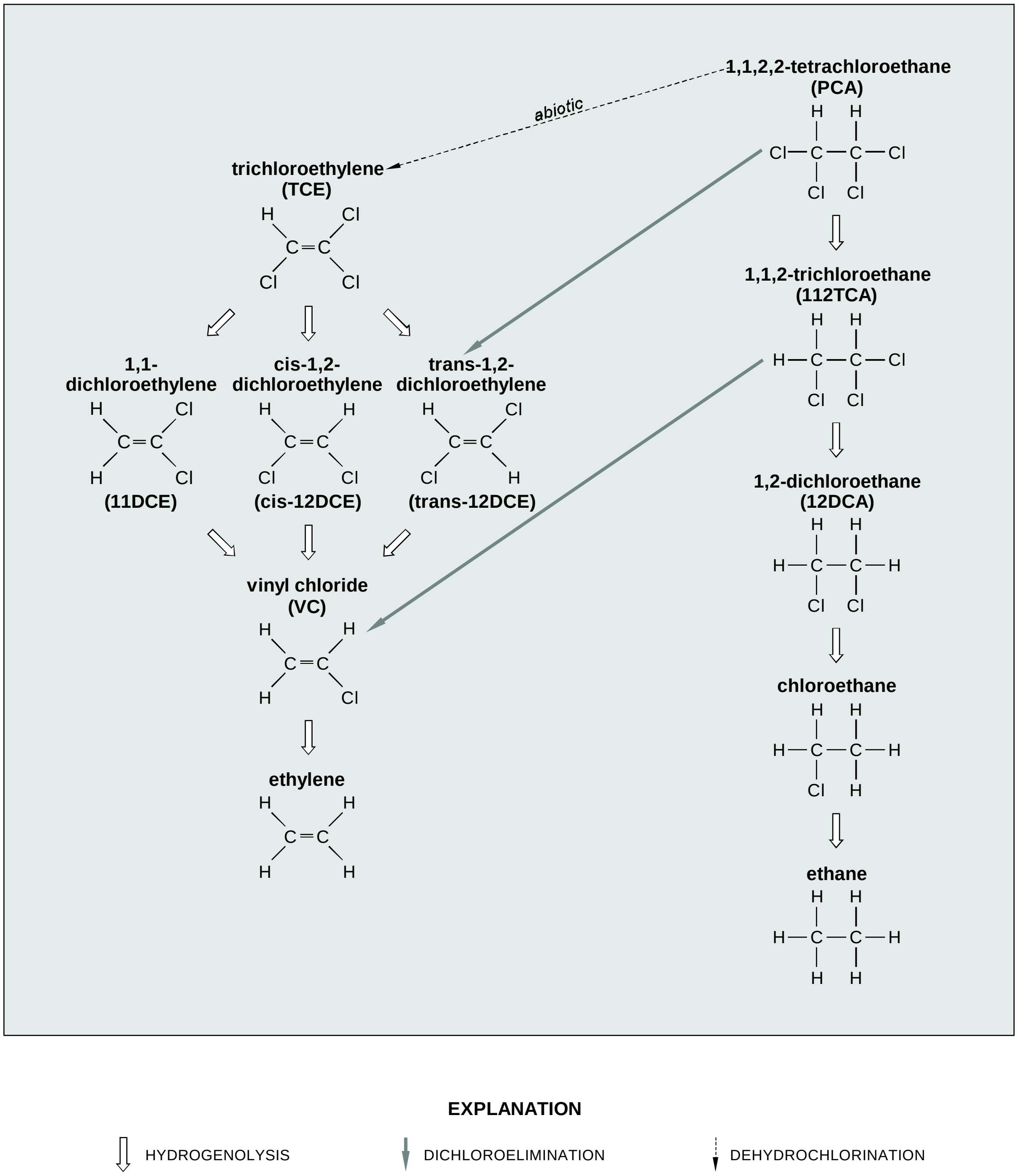


Figure 5. Anaerobic degradation pathways for trichloroethylene and 1,1,2,2-tetrachloroethane (modified from Chen and others, 1996, p.547, and Vogel and others, 1987, p.726).

to TCE and TCE to 12DCE, the rates were slower than those observed under similar laboratory conditions with methanogenic systems (Bagley and Gossett, 1990). The reduction process also is more complete under methanogenic conditions. Pavlostathis and Zhuang (1991) and Bagley and Gossett (1990) found that sulfate-reducing enrichment cultures could transform TCE to 12DCE, but further dechlorination to VC and ethylene did not occur. In contrast, many laboratory and field studies have reported TCE degradation to VC and, in some cases, to ethylene and ethane, under methanogenic conditions (for example, Vogel and McCarty, 1985; Belay and Daniels, 1987; McCarty and Semprini, 1994). Freedman and Gossett (1989) reported that acclimated methanogenic cultures could completely dehalogenate tetrachloroethylene and TCE to ethylene and carbon dioxide if sufficient electron donor, such as methanol or hydrogen gas, was supplied. In several ground-water studies at waste disposal sites where tetrachloroethylene or TCE were the parent compounds, detection of VC (Kastner, 1991; Lorah and Clark, 1996, p. 171) and ethylene (Fiorenza and others, 1994) coincided with the presence of methane.

Although anaerobic degradation of TCE has been fairly well-studied, few studies of PCA degradation under environmental conditions are known. PCA can be microbially degraded by hydrogenolysis, sequentially producing 1,1,2-trichloroethane (112TCA); 1,2-dichloroethane (12DCA); and chloroethane as daughter products (Bouwer and McCarty, 1983; Chen and others, 1996) (fig. 5). The final hydrogenolysis daughter product, chloroethane, can rapidly undergo abiotic hydrolysis to ethanol, which is a nontoxic end product (Vogel and McCarty, 1987). Two other transformation processes are possible for PCA--dihaloelimination, which is a second type of reductive dehalogenation reaction that releases two halide ions simultaneously, and dehydrochlorination, which is an abiotic elimination reaction (fig. 5). The relative rates and occurrence of the three possible transformation pathways of PCA in ground water are largely unknown.

Dihaloelimination is the reductive elimination of two adjacent chlorine atoms, forming an alkene. Dihaloelimination of PCA produces *cis*- and *trans*-12DCE. Dihaloelimination of PCA has been reported by transition-metal coenzymes that are often found in high concentrations in anaerobic bacteria (Schanke and Wackett, 1992) and by live cells in laboratory experiments with methanogenic municipal digester sludge (Chen and others, 1996). Dihaloelimination is also a possible transformation pathway for the 112TCA that can be produced by hydrogenolysis of PCA (fig. 5). Dihaloelimination of 112TCA produces vinyl chloride (Vogel and others, 1987; Chen and others, 1996).

The third possible transformation pathway for PCA is the production of TCE by abiotic dehydrochlorination. In a study with municipal digester sludge, hydrogenolysis, dihaloelimination, and dehydrochlorination simultaneously took place with PCA under methanogenic conditions. Dehydrochlorination of PCA, however, was only a minor reaction (removing 8 percent of the added PCA) in experiments with high concentrations of live cells, whereas dihaloelimination was the predominant degradation pathway (Chen and others, 1996).

CT undergoes hydrogenolysis to CF under various anaerobic conditions, including methanogenic, sulfate-reducing, iron-reducing, and dentrifying conditions (Bouwer, 1994; Picardal and others, 1995). Further biodegradation of CF to methylene chloride and carbon dioxide also has been reported under anaerobic conditions (Bouwer, 1994; Bagley and Gossett, 1995).

Aerobic Degradation

In early studies, TCE and other higher chlorinated hydrocarbons were found to be biologically transformed under anaerobic conditions but resistant to degradation under aerobic conditions (Alvarez-Cohen and McCarty, 1991). Wilson and Wilson (1985) first showed that TCE may be susceptible to aerobic degradation through use of soil microorganisms that were fed natural gas as a primary substrate in laboratory experiments. Other laboratory studies (for example, Little and others, 1988; Tsien and others, 1989) have since confirmed that methanotrophic bacteria, aerobic microorganisms that oxidize methane for energy and growth, are able to transform TCE and many other chlorinated hydrocarbons through cometabolism. Methane monooxygenase, the enzyme methanotrophs use to catalyze the initial step of methane oxidation, has a broad substrate specificity and can fortuitously oxidize chlorinated aliphatic hydrocarbons. Other oxygenases have been found to be capable of TCE transformation under aerobic conditions, including those used by microorganisms oxidizing toluene and other aromatic hydrocarbons, propane, ethylene, and ammonia. Most research to date has focused on the methanotrophs and the group of bacteria containing toluene oxygenase (McCarty and Semprini, 1994).

The aerobic degradation process is similar for these identified groups of microorganisms. With unsaturated chlorinated aliphatic hydrocarbons such as TCE, oxygenases add oxygen across the double bond to form epoxides. The epoxides are chemically unstable and can be transformed rapidly by abiotic hydrolysis to nonvolatile products, including aldehydes and acids. Heterotrophic microorganisms can further metabolize these products to carbon dioxide, chlorine, and water (Little and others, 1988). With saturated chlorinated aliphatic hydrocarbons such as CF, a hydroxyl group generally is substituted for one of the hydrogen atoms, producing compounds that are chemically unstable and decompose rapidly as for the unsaturated chlorinated aliphatics (McCarty and Semprini, 1994). Because of the unstable nature of the intermediate degradation products and the difficulty of obtaining mass balances, oxidation of chlorinated VOC's is extremely difficult to detect through field studies at contaminated sites and has not been demonstrated conclusively (Vogel, 1994).

The activity of methanotrophic bacteria in natural aerobic aquifers is believed to be too low to allow significant degradation of TCE and other organics, because concentrations of methane are commonly very low (Chapelle, 1993, p. 369). Aerobic degradation of TCE has been demonstrated, however, in a small-scale field study where methane and oxygen were injected into a shallow aquifer to manipulate the activity of methanotrophic bacteria (Semprini and others, 1990).

In contrast to anaerobic biodegradation processes where the degradation rate generally decreases as the degree of chlorination of the aliphatic hydrocarbon decreases, the less-chlorinated VOC's are more easily degraded through oxidation reactions under aerobic conditions than are the higher chlorinated compounds. 12DCE and VC oxidation rates, therefore, are relatively fast compared to TCE oxidation rates (Pfaender, 1990). In addition to cometabolic oxidation reactions, direct oxidation of vinyl chloride to carbon dioxide and water through use as a primary substrate has been demonstrated in laboratory experiments (Hartmans and deBont, 1992). Some highly chlorinated VOC's, including CT and tetrachloroethylene, are not known to be degraded under aerobic conditions (McCarty and Semprini, 1994). Of the chlorinated alkanes, 12DCA is the most susceptible to aerobic biodegradation, while 112TCA is less susceptible. Direct oxidation of 12DCA as a primary growth substrate has also been demonstrated, producing chloroethanol, which is then mineralized to carbon dioxide (Stucki and others, 1983; Wiedemeier and others, 1996, p. B3-24). No studies have been found in the literature that report aerobic microbial degradation of PCA through oxidation reactions.

Physical Processes--Dispersion and Sorption

Dispersion and sorption are two of the primary physical processes that could naturally attenuate ground-water contaminants. Hydrodynamic dispersion causes a contaminant plume to spread out in directions that are longitudinal and transverse to the advective direction of ground-water flow, so that the contaminants occupy a larger volume of the aquifer than would be expected only from advection. Dispersion, therefore, dilutes the concentrations of contaminants by mixing with less contaminated or clean ground water. Hydrodynamic dispersion is attributed to two processes--molecular diffusion and mechanical dispersion. Molecular diffusion is the migration of contaminants along concentration gradients from zones of higher to lower concentrations. Because molecular diffusion is the dominant dispersion mechanism only at extremely low ground-water velocities, it is often ignored in ground-water studies (Davis and others, 1993). Mechanical dispersion results from local variations in flow velocity that are caused by microscopic and macroscopic heterogeneities of the porous aquifer medium (Domenico and Schwartz, 1990). Longitudinal dispersion is the spreading of a solute in a direction parallel to the direction of ground-water flow, and transverse dispersion is spreading perpendicular to the direction of ground-water flow.

Sorption is the partitioning of dissolved solutes from the ground water onto the particles comprising the aquifer matrix. Although sorption retards movement of the contaminant plume relative to the advective ground-water-flow velocity, sorption is a reversible reaction so contaminants are not permanently removed from solution. Sorption is a complex process that can be caused by several mechanisms, including hydrogen bonding, chemisorption, and hydrophobic forces. Because of their nonpolar structure, chlorinated VOC's most commonly sorb through hydrophobic forces. Natural organic matter in the solid phase of sediments and soils, which has a pronounced hydrophobic character, is a better sorbent for hydrophobic, nonpolar contaminants than mineral surfaces, which are typically hydrophilic (Chiou and others, 1979; Schwarzenbach and Westall, 1981). In most ground-water systems, therefore, the organic fraction of the aquifer matrix controls sorption of organic contaminants, although clay minerals can also be an important sorbent. Distribution coefficients (K_d's) that describe the partitioning of hydrophobic contaminants between sorbed and dissolved phases have been found to correlate well with the fraction of organic carbon in the soil or sediment if the fraction of organic carbon is greater than about 0.1 percent (Schwarzenbach and Westall, 1981). Sorption to mineral surfaces, especially clay minerals, can be dominant in sediments with low organic carbon content.

The equilibrium distribution of organic contaminants between the sorbed and aqueous phases generally can be described by a linear sorption isotherm that is a special case of the Freundlich isotherm, because the number of sorption sites can be assumed to be very large compared to contaminant concentrations typically encountered in natural systems:

$$C_s = K_d C_w \quad , \qquad (1)$$

where

C_s = the amount sorbed to the solid phase (micrograms per kilogram);

C_w = the amount in solution (micrograms per liter); and

K_d = the distribution coefficient (slope of the isotherm, liters per kilogram) (Schwarzenbach and Westall, 1981; Lyman and others, 1982).

Although an equilibrium distribution between contaminant concentrations in the sorbed and aqueous phases is commonly assumed, numerous field and laboratory experiments recently have shown that sorption-desorption rate limitations can be significant. Sorption and desorption of hydrophobic organic compounds to sediments commonly entails an initially rapid and reversible equilibrium process, followed by slow reactions over a period of weeks or months because of relatively slow rates of mass transfer (Harmon and others, 1989; Brusseau and others, 1991). These slow reactions also result in a "desorption-resistant fraction" of contaminants that are often persistent in the environment (Carmichael and others, 1997). Several mechanisms have been suggested to account for this effect, including slow diffusion of the contaminants and absorption into solid organic matter, slow diffusion and entrapment within very small pores, and incorporation of the contaminant into natural organic matter through chemical oxidation reactions (Bosma and others, 1997).

Conceptual Model of Natural Attenuation in the Wetland Area

Although wetlands have been studied for their potential to treat nutrient- and metal-contaminated water (Hammer, 1989; Reddy and Gale, 1994), few studies are reported in the literature on the fate of organic contaminants in wetlands. Several studies have been conducted on the fate of organic contaminants in coastal wetlands in Louisiana (summarized by DeLaune and others, 1990). The contaminants that have been studied include petroleum hydrocarbons, chlorinated pesticides, pentachlorophenol (PCP), and polychlorobiphenyl (PCB). Sediment pH and redox potential were major factors controlling the persistence or degradation of the organic contaminants in bottom sediments and wetland sediments, and microbial degradation appeared to be the major removal mechanism. Swindoll and others (1995) presented preliminary evidence that anaerobic biodegradation is a major mechanism in decreasing concentrations of nitrobenzene and aniline in a wetland near a chemical manufacturing facility. Microbial degradation of hydrochlorofluorocarbons, possibly through a reductive dechlorination pathway, was observed in laboratory studies with anaerobic sediments from freshwater and salt marshes (Oremland and others, 1996). Biodegradation rates were more rapid in the freshwater sediments than in the salt marsh sediments. In addition, sorption of organic contaminants, including petroleum hydrocarbons, chlorinated solvents, and hexachlorobenzene, has been measured in a few laboratory studies on wetland sediments with high organic content (Rutherford and Chiou, 1992; Rutherford and others, 1992; Pardue and others, 1993). Rutherford and Chiou (1992) and Rutherford and others (1992) used peat as a model for natural soil organic matter in mechanistic studies of sorption processes.

For the tidal freshwater wetland along the West Branch Canal Creek at APG, it was hypothesized that natural attenuation of the chlorinated VOC's would be enhanced compared to the sand aquifer as the ground-water contaminants are transported upward through the wetland sediments. The contaminated aquifer was known to be aerobic upgradient of the wet-land because of the relatively rapid recharge rates (Lorah and Clark, 1996, p. 170) (fig. 6). Anaerobic biodegradation of the chlorinated VOC's through reduction reactions is unlikely to occur in the aerobic aquifer (Lorah and Clark, 1996), and a source of methane is not present in the aquifer to provide a substrate for methano-trophic bacteria that could degrade the VOC's under aerobic conditions. Significant sorption also is unlikely in the aquifer sediments because of their extremely low organic carbon content (Lorah and Vroblesky, 1989, p. 83). Although some volatilization could occur near the water table, only a relatively small proportion of the contaminants would be present near the water table in this aquifer that is about 40 ft thick upgradient of the wetland (Oliveros and Vroblesky, 1989, p.). Dispersion, therefore, might be the primary natural attenuation mechanism in the aerobic sand aquifer.

In contrast, anaerobic biodegradation, sorption, volatilization, and dispersion could all be significant mechanisms of natural attenuation in the wetland sediments. Anaerobic conditions exist in wetlands because oxygen diffusion is limited in waterlogged soils and because the high availability of natural organic substrates for microbial respiration causes rapid depletion of oxygen (Mitsch and Gosselink, 1986, p. 93). The amount of natural organic matter and oxygen typically varies over small depth intervals in wetland sediments, producing a wide range of redox zones where biodegradation reactions can occur. A large diversity and number of micro-organisms also are available to facilitate biodegradation in wetland sediments (Pardue and others, 1993). Biodegradation of the highly chlorinated VOC's that are the parent contaminants at the site (TCE, PCA, CT, CF) is known to occur under a range of anaerobic conditions (nitrate-reducing, iron-reducing, sulfate-reducing, methanogenesic) but is believed to be fastest and most complete under methanogenic conditions (McCarty and Semprini, 1994). In freshwater anaerobic sediments where sulfate concentrations are relatively low, 70 to 92 percent of organic carbon decomposition can be through methanogenesis (Capone and Kiene, 1988). Freshwater wetland sediments, therefore, could provide an ideal environment for natural attenuation of chlorinated VOC's through complete anaerobic degradation.

Wetlands are one of the few soil and ground-water environments where both anaerobic and aerobic degradation of chlorinated VOC's could

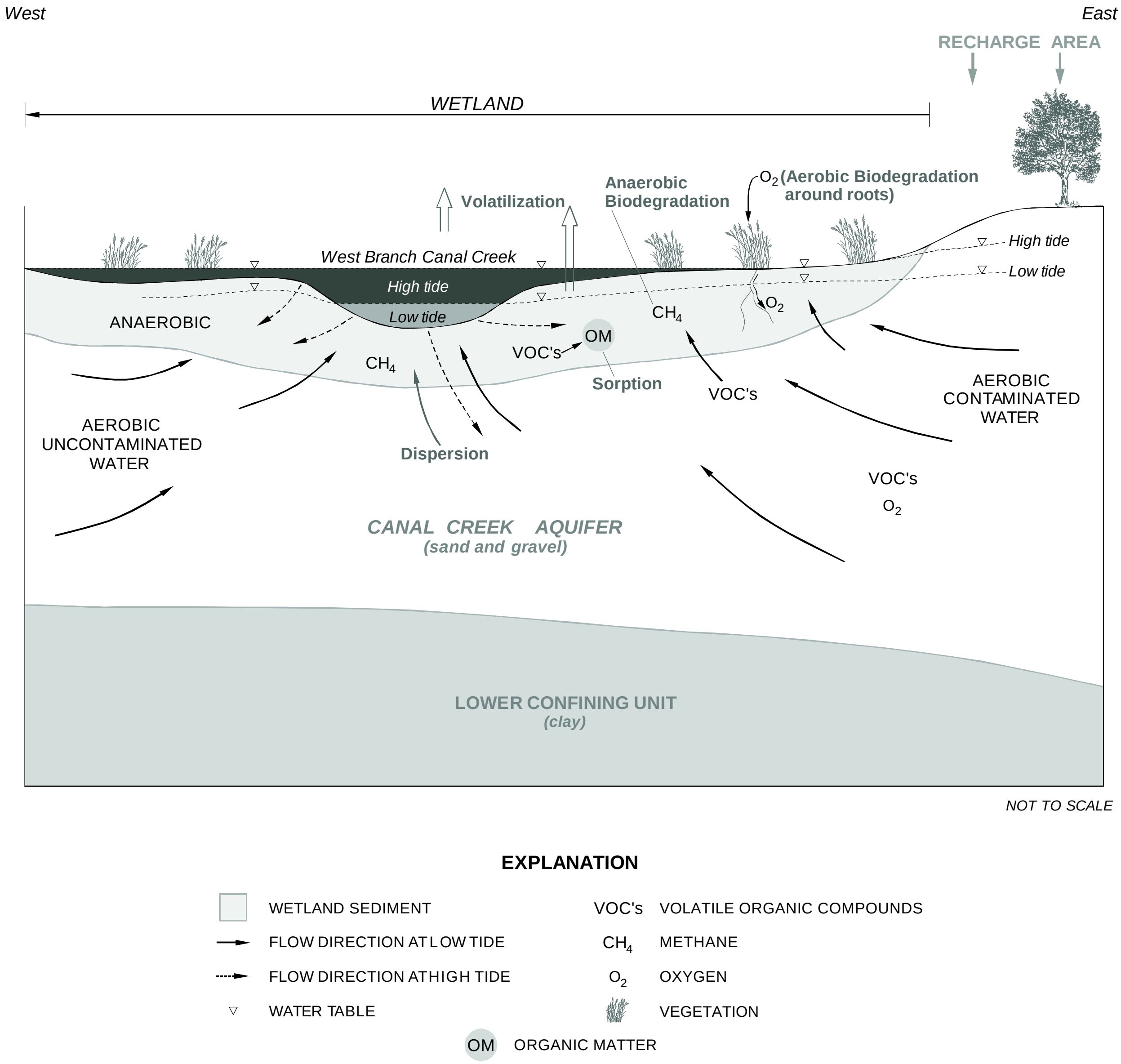


Figure 6. Conceptual model for the West Branch wetland site.

occur naturally (without engineered stimulation). Although wetland sediments generally have bulk anaerobic conditions, aerobic conditions are usually present in a thin layer of the surficial sediments in wetlands (Mitsch and Gosselink, 1986, p. 94). Methanotrophs, bacteria that have been associated with biodegradation of chlorinated VOC's under aerobic conditions, are generally most active at this interface between aerobic and anaerobic zones because both methane and oxygen are present. Methanotrophs also are active in the rhizoplane and root tissues of aquatic plants in wetlands (King, 1994). Many wetland plants transport oxygen from the atmosphere to their roots through an extensive system of internal gas spaces (Burke and others, 1988), creating suitable micro-environments for methanotrophs where oxygen is available from the roots and methane is available in the soil pore water (fig. 6). Thus, both methanogens and methanotrophs typically are active in wetland environments, and both anaerobic and aerobic biodegradation of the ground-water contaminants could possibly occur.

In addition, wetland sediments typically have a high content of natural organic matter that could sorb the hydrophobic parent contaminants. Interfacial processes such as sorption are further enhanced in wetlands because of the relatively high surface area available for reactions to occur relative to the water volume or flow (Pardue and others, 1993). Hydrologic conditions in the tidal wetland along the West Branch Canal Creek could greatly affect natural attenuation rates by affecting residence times and dispersion. During low tide, the primary direction of ground-water flow would be expected to be upward through the wetland sediments and the creek-bottom sediments (fig. 6). Some lateral flow in the wetland sediments toward the creek channel would also be expected. High tide, however, could reverse ground-water-flow directions, producing flow gradients vertically downward and laterally away from the creek channel in the wetland sediments. These changing flow gradients could prolong residence times of the contaminants in the wetland sediments, which would allow more time for attenuation reactions such as biodegradation to occur, and could increase dispersion and dilution of the contaminants. Infiltration of surface water through the creek channel and wetland surface during high tide could mix with the shallow ground water and further dilute contaminant concentrations.

METHODS AND DATA ANALYSIS

Monitoring Network

Installation procedures for the monitoring network are summarized in this section. During the reconnaissance phase of the wetland study, 17 drive-point piezometers were installed in April 1993 to collect preliminary hydrologic and water-quality data that would assist in locating the final ground-water-monitoring network (fig. 3). These initial piezometers, designated as "DP-" in the site number, have a 2-in.-diameter casing made of stainless steel and a 1-ft screened interval made of stainless-steel mesh with 60 micrometer (μm) pore diameter.

Collection of sediment cores and installation of the final monitoring network were completed during July 1994 to February 1995. Piezometer sites for the final monitoring network, designated as "WB-", are located mainly along two transects that are aligned along the general direction of ground-water flow in the aquifer, which is perpendicular to the creek channel (fig. 3). Two piezometer sites were also placed parallel to the creek channel near transect A-A' (WB-30 and WB-31 in fig. 3). At each site, three to seven drive-point piezometers were installed with screens placed at different intervals in the wetland and aquifer sediments; these are designated with a letter (beginning with "A" for the shallowest screen) after the site number. The piezometers installed for the final sampling network have 0.75-in.-diameter casing made of stainless steel and 6-in.-long screened intervals made of stainless-steel mesh with 150-μm pore diameter. An inner tube made of Teflon-lined polyethylene connects to the top of the screened interval, allowing withdrawal of samples that had minimum contact with the stainless steel. Additional 2-in.-diameter piezometers were also installed for continuous water-level monitoring with pressure transducers.

Other components of the monitoring network included a tide gage located near the bridge on Hanlon Road north of the study area, and a rain gage located upgradient of the eastern boundary of the wetland. Walkways and a bridge across the creek by site WB-27 were constructed along the transects before installation of the final monitoring network to minimize disturbance of the wetland sediments and to allow access to sites at high tide.

Characterization of the Hydrogeology

Continuous sediment cores were collected at each of the 18 sites that were used for the final ground-water sampling network to obtain lithologic and mineralogical data (Olsen and others, 1997). Total organic carbon content was also determined for selected sediment samples. Head distributions along the transects were determined from 26 sets of synoptic water-level measurements that were made during 1995-96 (Olsen and others, 1997). Each synoptic set consisted of measurements made during periods of low and high tides on the same day. Continuous water-level measurements also were made in selected piezometers and the tide gage, using pressure transducers and automatic-recording devices.

Three methods were used to calculate hydraulic conductivities of the wetland and aquifer sediments. Data obtained from slug tests, which were conducted from January through March of 1996, were analyzed in the program AQTESOLV (Fetter, 1994, p. 266-268) to calculate hydraulic conductivities using the Bouwer-Rice method (Fetter, 1994, p. 251-256). Slug tests were performed at 10 different sites and at varying depths. Secondly, analysis of grain-size distribution (Olsen and others, 1997) were used to calculate hydraulic conductivities at five sites. These values were calculated from an empirical method devised by Hazen (Fetter, 1994, p. 99). A third procedure that was used to calculate hydraulic conductivity is based on the response of water levels in piezometers to the cyclic tidal fluctuations in creek stage. Hydrographs for these determinations were generated from unpublished data (data on file in the Maryland-Delaware-D.C. District office, USGS, Baltimore, Md.) that were collected from the tide gage on the West Branch Canal Creek and from pressure transducers in selected piezometers.

Ground-water flow through sections A-A' and C-C' was calculated using Darcy's law (Fetter, 1994, p. 94-95):

$$Q = \frac{-KA\Delta h}{\Delta l}, \qquad (2)$$

where

Q is ground-water flow (L^3T^{-1});

K is hydraulic conductivity (LT^{-1});

A is the cross-sectional area (L^2);

Δh is change in head along the length Δl (L); and

Δl is the length (L).

An average value of hydraulic conductivity was calculated along a flow path through the sections. Where ground-water flow was vertical, the vertical component of hydraulic conductivity also was calculated, using the equation (Lee and Fetter, 1994, p. 127-128):

$$K_z = \frac{b}{\Sigma\left(\frac{b_i}{K_i}\right)}, \qquad (3)$$

where

K_z is the mean vertical hydraulic conductivity (LT^{-1});

b is the total length of the flow line (L);

b_i is the length of the ith increment (L); and

K_i is the horizontal hydraulic conductivity of the ith increment (LT^{-1}).

The specific discharge (Darcian velocity) and the average linear velocity (seepage velocity) were calculated from (Fetter, 1994, p. 145):

$$q = \frac{Q}{A}, \qquad (4)$$

$$v = \frac{Q}{nA}, \qquad (5)$$

where

q is specific discharge (LT^{-1});

v is average linear velocity (LT^{-1}); and *n* is effective porosity (dimensionless).

To calculate the total discharge along the sections, flow nets were constructed. In flow-net analysis, the total discharge per unit width of the section is assumed to be the same in all flow tubes, which requires the assumptions that the aquifer is homogeneous, isotropic, and fully saturated and that the potential field does not change with time (Lee and Fetter, 1994, p. 53-60). Although these assumptions are not strictly met, the flow-net analysis is useful in obtaining a rough estimate of the total discharge. The total discharge in a tube on the flow net is

$$Q_t = qw \ , \tag{6}$$

where

Q_t is the total discharge in flow tube per unit width of aquifer (L^2T^{-1}); and

w is the width of flow tube (L).

Ground-Water and Surface-Water Sampling and Analysis

Samples collected after installation of the final piezometer network primarily are discussed in this report. Water samples were collected from 87 of the 0.75-in.-diameter piezometers during June-October 1995. About 28 to 30 selected piezometers were then sampled in March-April 1996, June 1996, and August 1996 to evaluate seasonal effects on ground-water quality. A sampling run also was begun in November 1995 but was not completed because of U.S. Government shutdowns. One of the reconnaissance-phase piezometers, DP-1A, was included in the seasonal sampling. In addition, the two wells at site CC-27, which are 4-in.-diameter monitoring wells that were installed during the previous (1985-92) investigation, were resampled in July 1993 and August 1996 as part of the wetland study.

Piezometers screened in the aquifer generally were purged and sampled using a peristaltic pump fitted with tygon tubing. Because piezometers screened in the wetland sediments generally had low recovery rates, bailers were used for purging and sampling. Stainless-steel or Teflon bailers were used to purge and sample the 0.75-in.-diameter and 2-in.-diameter piezometers, respectively, in the wetland sediments. Specific conductance, salinity, water temperature, and turbidity were monitored during purging. In piezometers with rapid water-level recovery rates, samples were collected when these parameters stabilized (usually after 1.5 to 2 casing volumes of water had been removed). If a piezometer went dry and recovery took more than 8 hours after removal of one casing volume of water, sampling was begun the next day or as soon as water levels had risen at least 1 ft above the screen. Samples for different constituents were then collected over several days, and sometimes over more than a week, in these piezometers. Water levels were maintained above the top of the screened interval during purging and sampling.

Water temperature, specific conductance, salinity, turbidity, pH, and dissolved oxygen, were measured in the field immediately after collection of unfiltered sample. Alkalinity was measured in the field immediately after collection and filtration of sample through a 0.45-micrometer membrane filter. Water temperature was measured using thermistor thermometers that had a precision of 0.2 ^{o}C or by using alcohol-filled thermometers marked in increments of 0.5 ^{o}C. Specific conductance, salinity, and turbidity were measured with commercial meters that were checked daily with standard reference solutions. The pH was determined with a commercial pH meter that was equipped with a gel-filled combination pH electrode and temperature-compensation probe and calibrated with two pH buffers. Alkalinity was determined by potentiometric titration of continuously stirred samples using 0.16 N sulfuric acid to titrate to a pH of about 3.8. Alkalinity was calculated by locating the maximum of the first derivative of the curve generated from pH as a function of the titrant volume. Dissolved-oxygen concentrations were measured by use of a modified Winkler colorimetric method (Baedecker and Cozzarelli, 1992) for those piezometers that contained sufficient water volume to fill a 60-mL bottle and allow it to overflow at least 1.5 times its volume. For many piezometers screened in the wetland sediment, dissolved oxygen was not measured because of insufficient water volumes.

Water samples for analyses of redox-sensitive constituents and VOC's generally were collected first, followed by collection of samples for major ions and trace metals. Redox-sensitive constituents, in addition to dissolved oxygen, that were determined on each of the four sampling periods included manganese, ferrous and ferric iron, sulfide, and methane. In addition, ammonia was determined during the March 1996 sampling period. Samples were analyzed by project staff in the field, by project staff at an on-site laboratory that was located in a mobile trailer owned by USACEHR, or by the USGS National Water Quality Laboratory (NWQL). All samples were stored on ice in the field and during shipping to NWQL and then refrigerated until analyzed.

Filtered samples (0.45 µm) were collected for manganese analysis in polyethylene bottles and acidified immediately to pH less than 2.0 with ultrapure nitric acid. Manganese concentrations were determined at NWQL using inductively coupled argon plasma spectroscopy. Samples for analysis of total dissolved iron were collected and analyzed by NWQL in the same manner as manganese. Ferrous iron and total dissolved iron concentrations, however, also were determined in samples filtered through 0.1-µm filters and immediately treated in the field with reagents specified by the colorimetric bipyridine technique (Brown and others, 1970; Baedecker and Cozzarelli, 1992). Dissolved ferrous and total iron samples were refrigerated for as long as 2 weeks, until the absorbance was measured at the on-site laboratory on a Bausch and Lomb Spectronic 21 spectrophotometer at a wavelength of 520 nm. Ferric iron concentrations were calculated by difference. Only concentrations determined on 0.1-µm filtered samples and analyzed using the bipyridine method are discussed in this report.

Initially during the June-October 1995 sampling period, unfiltered sulfide samples were collected in 10-mL glass syringes and analyzed using the colorimetric method outlined by Baedecker and Cozzarelli (1992). Sulfide samples were reacted in the field with diamine and ferric chloride in an acidic reagent solution to form a methylene blue color complex and were then analyzed within 1 week on a Bausch and Lomb Spectronic 21 spectrophotometer at a wavelength of 670 nm. During the later half of the June-October 1995 and subsequent sampling periods, sulfide was determined on unfiltered samples by a similar colorimetric method, but reagents were obtained in sealed ampules from CHEMetrics (Calverton, Virginia). Samples were analyzed in the field using the CHEMetrics System 1000 kit that includes a portable spectro-photometer. Analyses of duplicate samples showed that the two sulfide methods gave concentrations that agreed within 10 percent. During the March 1996 sampling period, ammonia concentrations also were determined on unfiltered samples from selected piezometers using a CHEMetrics System 1000 colorimetric method.

Following the method outlined by Baedecker and Cozzarelli (1992) for methane determination, unfiltered water was drawn directly from the sampling device into a 10-mL glass syringe fitted with a three-way stopcock. The methane samples were immediately transferred to sealed serum bottles that contained mercuric chloride as a preservative and that had been flushed with nitrogen gas prior to sample collection. Methane samples were analyzed by gas chromatography with a flame ionization detector at the on-site laboratory.

For collection of VOC's, two or three glass vials were filled for each piezometer with a slow steady stream of water from the sampling device to minimize aeration. The vials were allowed to overflow with about three volumes of water and then immediately sealed with caps lined with a Teflon septum. Concentrations of VOC's were determined by purge and trap capillary gas chromatography/mass spectrometry (GC/MS). During June-October 1995, VOC samples were collected in 40-mL vials and shipped to NWQL for analysis. During subsequent sampling periods, VOC's were collected in 8- or 12-mL vials and analyzed at the on-site laboratory. The analytical method used at both laboratories is equivalent to USEPA Method 524.2 and is given in Rose and Schroeder (1995). Split samples that were analyzed at the two laboratories generally agreed within 20 percent. This is only slightly higher than the average relative standard deviations for duplicate pairs analyzed at each laboratory, which were 15 and 17 percent (Olsen and others, 1997).

Water samples collected for major cations and trace metals were filtered through 0.45-µm membrane filters into polyethylene bottles and acidified inmediately to pH less than 2.0 with ultrapure nitric acid. Samples collected for major anions were filtered through 0.45-µm membrane filters but were not treated with preservatives. Concentrations of major anions were determined by ion chromatography at the NWQL. Concentrations of major cations and trace metals were determined at the NWQL by inductively coupled argon plasma spectroscopy, except for the following constituents: potassium and arsenic (atomic absorption), aluminum and boron (direct-current plasma), and lead (graphite furnace atomic absorption). In addition, samples were collected for analysis of total dissolved organic carbon (DOC) during the June-October 1995 sampling period. Samples were filtered through 0.1-µm membrane filters into 12-mL glass vials that contained mercuric chloride as a preservative and sealed with Teflon-lined septa. Samples were then analyzed at the University of Virginia on an organic carbon analyzer. The method that was used requires acidification and sparging of the sample to remove inorganic carbon, which also removes VOC's. Thus, these organic contaminants are not included in the DOC analyses.

In addition to ground water collected from the piezometers, water samples were obtained over 1-in. intervals in the wetland sediments by use of porous membrane samplers that are commonly called "peepers." Six peepers were built of Lexan following the general design originated by Hesslein (1976) for studies in bottom sediments of lakes. The peepers are constructed of three sheets of strong polycarbonate (Lexan). The middle Lexan sheet is 0.6 in. thick and contains the sample chambers; two 0.12-in.-thick sheets are overlays that hold the porous membrane over the sample chambers. Each peeper is 24 in. long (excluding a handle used for installation) by 7.5 in. wide and contains 21 rows of sample chambers with 2 chambers in each row. The sample chambers were filled with deionized water that was held in the chambers between the porous membrane and the overlays. The porous membrane (HT Tuffryn, Gelman Sciences, Ann Arbor, Michigan) was made of polysulfone and had 0.2-µm pore size. The peepers were manually pushed vertically into the wetland sediment and allowed to equilibrate with surrounding porewater for approximately 3 weeks. In theory, constituents in the surrounding porewater should diffuse into the peeper chambers until concentrations inside and outside the chambers are equal. Before installation in the wetland sediments, the prepared peepers were placed in a large container filled with deionized water and bubbled contin-uously with nitrogen gas for 12 to 18 hours to remove oxygen from the water in the peeper chambers. After equilibration in the sediment, the peepers were removed from the sediment, and samples were immediately collected from the chambers using glass syringes. Because sample sizes obtained from the peepers were very small (about 11 mL from each chamber), only VOC's and methane were measured. These analyses were done at the on-site laboratory using the same methods discussed above for the piezometers. The peepers were installed near selected piezometer sites during each sampling period except August 1996.

Surface-water samples were collected using an ISCO automatic water sampler with the pump intake located near the creek bottom by site WB-27 (fig. 3). Because previous surface-water samples that were collected along West Branch Canal Creek [by immersing 40-mL glass vials several inches below the surface of the water and filling with minimal aeration] showed low or undetectable concentrations of VOC's (Lorah and Clark, 1996), VOC concentrations were not determined in surface-water samples during this study. Instead, samples for inorganic analyses were collected and used primarily to evaluate the effects of surface-water infiltration and dilution on ground-water chemistry. Surface-water samples were collected a total of six times between June 1995 and March 1996; each time, samples were collected every 2 or 4 hours over a 3-day period to obtain concentrations of major inorganic constituents over tidal cycles. At the end of each 3-day period, the samples were unloaded from the ISCO and filtered through 0.45-µm membrane filters into polyethylene bottles for determination of major ions and selected trace metals. Samples for major anions, major cations, and trace metals were treated as described above for the groundwater samples and sent to NWQL for analysis. Alkalinity, specific conductance, and salinity were measured in the field, using the methods described above, at a few time intervals during the initial surface-water sampling periods.

Microcosm Experiments

Anaerobic Experiments

During May-June 1996, microcosm experiments were conducted under anaerobic conditions to determine the potential degradation rates of two of the primary parent contaminants, TCE and PCA, in the wetland sediments and to identify degradation (or daughter) products. The various treatment sets prepared for these microcosm experiments are summarized in table 1. The treatments included an unamendend control; two sets of microcosms amended with different initial concentrations of TCE; one set amended with PCA; and, one set amended with TCE and high sulfate concentrations (10 mM) to induce sulfate-reducing conditions. Methanogenic conditions were expected to develop rapidly in all microcosms that were not amended with sulfate. A compound known to be a specific inhibitor of methanogenesis, 2-bromoethanesulfonic acid or BES (Oremland and Capone, 1988), was added to one set of TCE-amended microcosms to evaluate whether biodegradation would stop with inhibition of methanogens. Sterile controls were constructed for each treatment so that abiotic removal of the VOC's could be distinguished from microbial reactions.

***Table 1**. Treatments used during anaerobic microcosm experiments at the West Branch study area, Aberdeen Proving Ground, Maryland, May-June 1996*

[Trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA) concentrations are given in micromoles per liter, followed (in parentheses) by the concentration in micrograms per liter; BES = 2-bromoethanesulfonic acid; mmol/L, millimoles per liter]

Experiment name	Amendments [planned TCE or PCA concentration at Day 0]	Estimated TCE or PCA concentration at Day 0
E1	Unamended	0
E2	TCE [3.8 (500)]	3.0 (400)
E3	TCE [7.6 (1,000)]	7.5 (990)
E4	PCA [3.0 (500)]	2.9 (480)
E5	TCE [7.6 (1,000)]; 10 mmol/L sulfate	7.5 (990)
E6	TCE (7.6 (1,000)]; 30 mmol/L BES	7.5 (990)
Sterile Controls		
SE2	TCE [3.8 (500]; 1% formaldehyde	3.0 (400)
SE3	TCE [7.6 (1,000)]; 1% formaldehyde	7.5 (990)
SE4	PCA [3.0 (500)]; 1% formaldehyde	2.9 (480)
SE5	TCE [7.6 (1,000)]; 10 mmol/L sulfate; 1% formaldehyde	7.5 (990)

Microcosms were constructed in 162-mL serum bottles using a 1.5:1 volumetric ratio of ground water to wetland sediment. Ground water from the wetland sediments was collected in 1-L glass bottles from a piezometer at site WB-24 (fig. 3) during the week prior to microcosm construction. The ground water was homogenized in a large polyethylene bucket, and the pH was tested immediately prior to microcosm construction. The initial water pH was approximately 6.2, which was consistent with the pH measured in this piezometer during previous sampling events (Olsen and others, 1997). Wetland sediment was collected near DP-6 and

WB-30 (fig. 3) from a depth of 0.5 to 10 in. below land surface and sieved to remove particles greater than 0.187 in. (4.75 mm). Sieving and microcosm construction were done under a nitrogen atmosphere in a disposable glove-bag, and the bottles were then sealed with Teflon-lined rubber septa and aluminum crimp caps. Stock TCE and PCA solutions were made from neat chemicals (Supelco, Bellefonte, Pa.) and added to the microcosms using gas-tight syringes to give the planned initial dissolved concentrations (table 1). Concentrations of the stock solutions were analyzed at the on-site laboratory by GC/MS prior to amending the microcosms and used to estimate concentrations in the microcosms at day 0 (the day the microcosms were amended with TCE or PCA). Sterile controls were prepared with filtered ground water (0.1 µm) and 1 percent by volume of formaldehyde to inhibit microbial growth.

Microcosms were stored upside down in the dark at 19 °C, which was the approximate temperature of the wetland ground water during the summer (Olsen and others, 1997). The microcosms were gently mixed approximately every day by inverting the bottles several times. Duplicate serum bottles were sacrificed at selected time intervals, and the water was analyzed for VOC's and methane at the on-site laboratory, as described above for ground-water samples.

Biodegradation rates were calculated by a first-order approximation. First-order decay is described by the following ordinary differential equation:

$$\frac{dC}{dt} = kt \qquad (7)$$

where

C is the concentration remaining at time t [M/L^3], and
k is the first-order rate constant [1/T].

Solving this differential equation yields:

$$C = C_o e^{-kt} \quad , \qquad (8)$$

where

C_o is the concentration at day O.

The rate constant k can be determined from the slope of a linear regression of the natural logarithm of the concentration remaining in the non-sterile microcosms against time of incubation (t). If significant losses (greater than 5 percent) were measured in the sterile microcosms, this concentration was subtracted from the concentration in the non-sterile microcosms to adjust for abiotic losses before the first-order rate constant was calculated.

Aerobic Experiments

During November 1996 to January 1997, the potential aerobic biodegradation rates of TCE, *cis*-12DCE, *trans*-12DCE, and VC were evaluated using surficial wetland sediment and ground water that was incubated under aerobic conditions. Microcosms were constructed in dark glass 130-mL bottles using 35 mL of ground water and 25 mL of wetland sediment (table 2). Ground water from the wetland sediments was collected from site WB-24 about 1 week prior to microcosm construction. The ground water was homogenized in a large glass beaker, and the pH was tested immediately prior to microcosm construction. The inital water pH was approximately 6.2. Sediment was collected near sites DP-6 and WB-30 from a depth of about 0 to 5 in. below land surface.

Some microcosms were constructed using sediment as it was collected, which included plant roots. For comparison to microcosms constructed with root material, some microcosms were constructed using sediment that had been sieved to remove particles greater than 0.187 in. (4.75 mm) and all visible roots (table 2). Sieving and microcosm construction were done under ambient air. The bottles were then sealed with Mininert caps that are designed to allow repeated withdrawals of headspace samples from the same bottle. Stock solutions of TCE, *cis*-12DCE, *trans*-12DCE, and VC were mixed in methanol from standards (Supelco, Bellefonte, Pa.) and added to the microcosms using gas-tight syringes to give the planned initial dissolved concentrations. Duplicate microcosms were prepared for each treatment.

Table 2. *Treatments used for aerobic microcosm experiments at the West Branch study area, Aberdeen Proving Ground, Maryland, November-December 1996*

[DME, dimethyl ether; TCE, trichloroethylene; *cis*-12DCE, *cis*-12-dichloroethylene; *trans*-12DCE, *trans*-12-dichloroethylene; VC, vinyl chloride. Concentrations of methane and DME are in percent by volume of headspace. Concentrations of formaldehyde are in percent by volume of water. Aqueous concentrations of TCE, *cis*-12DCE, *trans*-12DCE, and VC that were estimated to be in the microcosms at day 0 are given in micrograms per liter]

Experiment name	**Sieved**	**Methane (percent)**	**DME (percent)**	**Formaldehyde (percent)**	**TCE**	***cis*-12DCE**	***trans*-12DCE**	**VC**
brt-1	no	1			1,000			
brt-2	no	3			1,000			
brt-3	no	1	10		1,000			
bnt-1	yes	1			1,000			
bnt-2	yes	3			1,000			
bnt-3	yes	1	10		1,000			
brv-1	no	1				1,000	1,000	600
brv-3	no	1	10			1,000	1,000	600
bnv-1	yes	1				1,000	1,000	600
bnv-3	yes	1	10			1,000	1,000	600
Sterile								
bsrt-1	no	1		1	1,000			
bsrt-2	no	3		1	1,000			
bsnt-1	yes	1		1	1,000			
bsnt-2	yes	3		1	1,000			
bsrv-1	no	1		1		1,000	1,000	600
bsnv-1	yes	1		1		1,000	1,000	600

Before adding the VOC solutions, methane (99 percent pure, Scott Specialty Gases) was added to the headspace of the microcosms at concentrations of either 1 or 3 percent of headspace volume to provide a substrate for methanotrophic bacteria (table 2). In addition, dimethyl ether (99.6 percent pure, Matheson Gas Products), which is a specific inhibitor of methanotrophic activity, was added to several sets of microcosms (Oremland and Culbertson, 1992). Sterile controls were prepared with filtered ground water (0.1 µm) and 1 percent by volume of formaldehyde to inhibit microbial growth.

Microcosms were stored upside down in the dark at 19 °C, as for the anaerobic experiments. The microcosms were gently mixed approximately every day by inverting the bottles several times. Approximately every 3 days, oxygen gas (at least 99.6 percent pure, Roberts Oxygen) was added to all microcosms at concentrations of 10 percent by volume in the headspace to attempt to maintain aerobic conditions. Methane also had to be added to the microcosms as it was consumed. Headspace samples (2 mL total) were withdrawn at selected time intervals and injected directly into the GC/FID and GC/MS for analysis of methane and VOC's, respectively, at the on-site laboratory. The concentration of the VOC's in the water was calculated using the following Henry's Law constants (K_h's) for TCE, *cis*-12DCE, *trans*-12DCE, and VC, respectively, at 25 °C: 0.4173, 0.179, 0.3814, 1.0836 (Mackay and others, 1993). First-order degradation rate constants were calculated as described above for the anaerobic microcosm experiments.

Sorption Measurements

To evaluate the possible significance of sorption in the wetland sediment, the concentrations of VOC's were measured in selected sediment samples collected during installation of the final monitoring network. Samples were taken from the center of 3-in.-diameter split-spoon cores and transferred directly to 40-mL VOC vials, leaving minimal headspace. The samples were shipped overnight to NWQL, where a subsample from each vial was extracted with methanol according to USEPA Method 8240 and analyzed by purge and trap capillary GC/MS according to USEPA Method 524.2. Percentage of moisture was determined, and the sample results were quantitated based on a dry weight.

In addition, equilibrium distribution coefficients (K_d's) were estimated by conducting batch tests to determine 24-hour equilibrium isotherms for selected contaminants (PCA, *cis*-12DCE, *trans*-12DCE, and VC). Wetland sediment and ground water were collected near the same locations as used previously in the microcosm experiments. Sediment from both the upper and lower wetland units was collected in approximately equal proportions. The sediment was sieved to remove particles greater than 0.187 in. (4.75 mm), homogenized by manual stirring, spread in a shallow stainless-steel pan, and allowed to air dry for 72 hours. The batch tests were constructed without headspace in dark-glass 40-mL VOC vials. After weighing each empty vial, 25 g of sediment was added before filling with filtered (0.2 µm) ground water. The vials were capped and reweighed. The difference in weights were used to calculate the volume of water in each vial and adjust the measured concentrations of VOC's. Two sets of blanks were constructed using only deionized water and no sediment.

Stock solutions of the VOC's were made using neat chemicals or standards in methanol (Supelco, Bellefonte, PA) and were added to the batch vials by injection through the Teflon-lined septa. Duplicate vials (sometimes triplicates) were injected with one compound at one concentration level, except the batch tests for *cis*-12DCE and *trans*-12DCE were prepared with stock solutions containing equal concentrations of the two constituents. Nine concentration levels ranging from about 10 to 100,000 µg/L were used for PCA, and five concentration levels ranging from about 10 to 250 µg/L were used for *cis*-12DCE, *trans*-12DCE, and VC. The vials were then placed upside down on a shaker, covered with aluminum foil to block out light, and allowed to shake gently (100 rotations per minute) for 24 hours at room temperature (23 ° to 24 °C). One set of blanks were spiked with the VOC's and then sampled immediately to establish actual initial concentrations, whereas the second set of blanks was placed on the shaker and sampled after 24 hours.

After 24 hours, the vials were centrifuged for 15 minutes at 2,000 rotations per minute to separate the solution and sediment and were then opened to decant solution into 8-mL glass vials for analysis of dissolved VOC concentrations. Aqueous concentrations of the VOC's were measured at the on-site laboratory using purge-and-trap GC/MS, as described above for ground-water samples.

Sorbed concentrations of VOC's (C_{sorbed}) in each vial were calculated from:

$$C_{sorbed} = (M_i - M_w)/M_s \quad , \qquad (9)$$

where

M_i is the initial mass of solute added to the vial;

M_w is the mass of solute measured in the water after 24 hours; and

M_s is the mass of sediment in the vial.

The sorbed concentrations were plotted versus the aqueous concentrations for each solute, and the distribution coefficient (K_d) was calculated by linear regression through the origin. The K_d is the slope of the linear isotherm.

NATURAL ATTENUATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS

Three lines of evidence ideally are used to support the occurrence of natural attenuation of organic contaminants (Wiedemeier and others, 1996, p. 1-6): (1) observed reductions in contaminant concentrations along a flowpath downgradient from the contaminant source; (2) geochemical and hydrologic data that demonstrate appropriate redox conditions for biodegradation, provide field evidence of the occurrence of biodegradation, and allow calculation of biodegradation rates at the field scale; and (3) laboratory microbiological data that supports the occurrence of biodegradation and gives potential rates. Results from all three lines of evidence are discussed here, demonstrating that natural attenuation of the chlorinated VOC's is occurring in the wetland sediments along the West Branch Canal Creek at APG.

Final calculations of biodegradation rates at the field scale, however, will not be done until a planned ground-water tracer test and volatilization experiments are completed. Biodegradation rates at the field scale often are extremely difficult to obtain because accurate determination of contaminant residence time and mass balance along the flowpath is required. Complex hydrogeology, the absence of a natural conservative tracer, and the occurrence of natural attenuation mechanisms besides biodegradation can complicate these determinations. Much of the information ultimately required to determine field biodegradation rates is discussed here, including characterization of the hydrogeology and evaluation of the major biodegradation pathways and sorption rates. Although other natural attenuation processes can be critical in reducing the concentrations, and thus the toxicity of contaminants, biodegradation has been emphasized to support natural attenuation as a remediation method (Wiedemeier and others, 1996, p. 1-7).

Characterization of the Hydrogeology

Characterization of the hydrogeology is needed to understand the distribution and movement of contaminants and to quantify the extent of natural attenuation. This section discusses the lithology and mineralogy of the geologic units delineated in the study area, describes the head distributions and ground-water-flow directions, and provides estimates of flow velocities and total discharge to the wetland and creek.

Lithology and Mineralogy

The Canal Creek aquifer is about 40 to 45 ft thick in the study area (figs. 7 and 8). The aquifer sediments are of fluvial origin and consist of medium- to coarse-grained sand and gravel interfingered with thin layers or lenses of clay, fine sand, and silt. One layer of clayey silt or clay interbedded with fine sand ranged from about 1 to 5 ft in thickness and seemed to be fairly continuous and extensive. This layer was shallow in the aquifer at a depth of 18 to 24 ft below mean sea level along the entire C-C' and part of the A-A' transect. Orange to yellow iron staining is common in the sand and gravel of the aquifer, and iron mineralization often occurs as small nodules and cemented layers. A thin continuous layer of cemented sand was present near the bottom of the aquifer along the C-C' transect. The mineralogy of the aquifer sediments consists of predominantly quartz with trace amounts of mica, kaolinite, plagioclase, goethite, and hematite (Olsen and others, 1997). Upgradient from the wetland, the aquifer is overlain by a mixture of recent fill material and the upper confining unit (figs. 7 and 8).

Wetland sediments overlie the Canal Creek aquifer within the current wetland boundary. In addition, organic-rich clay and peat were found at site WB-20 at a depth of 12.0 to 12.6 ft, indicating that the wetland may have once extended at least 200 ft upgradient of the current wetland boundary. The wetland sediments typically consist of two distinct layers that have a combined thickness of about 6 to 12 ft in the study area-- an upper unit of peat mixed with variable amounts of clay and silt and a lower unit of silty to sandy clay or clayey sand (figs. 7 and 8). In addition, a thin unit of sand and gravel lies between the two wet-land sediment units in the creek channel and is

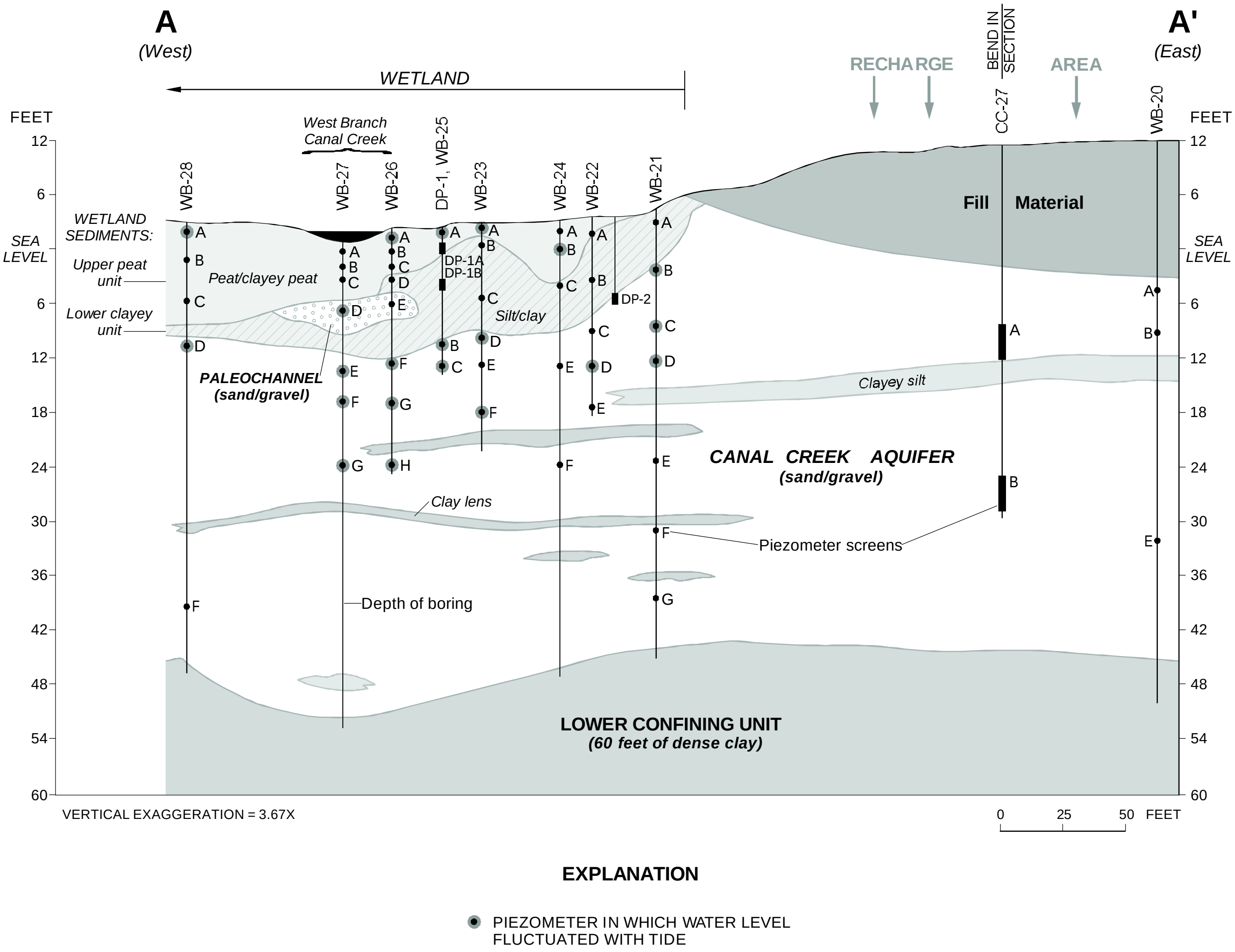


Figure 7. Section A-A' showing the hydrogeology and locations of piezometer screens, and indicating those piezometers in which water levels were affected by tidal fluctuations.

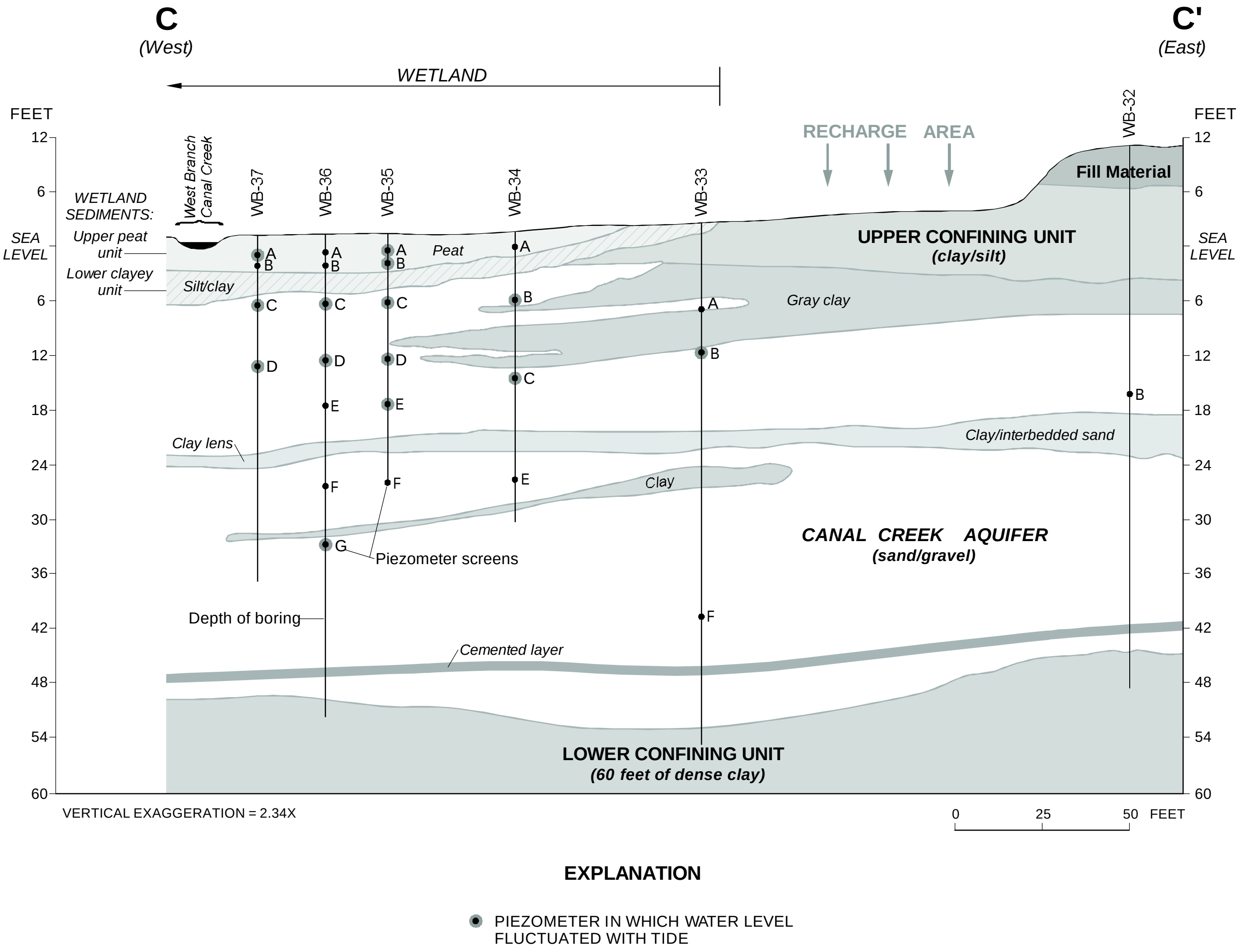


Figure 8. Section C-C' showing the hydrogeology and locations of piezometer screens, and indicating those piezometers in which water levels were affected by tidal fluctuations.

probably a deposit from a previous channel (fig. 7). Typically, the wetland sediments have a grayish-brown, gray, or black color that indicates a reducing environment, although orange or red, narrow oxidized zones are sometimes visible around roots. Roots were visible in sediment cores to depths as great as 12 ft, which is the approximate maximum thickness of the wetland sediments. The wetland sediments are thicker and more heterogeneous along transect A-A' than C-C'. The mineralogy of the upper peat unit typically consists of major amounts of quartz and organic material and minor amounts of mica, feldspars, chlorite, kaolinite, and pyrite. In addition, trace gypsum was detected in peat at sites near and beneath the creek channel (sites 27, 28, and 36 in figs. 7 and 8). The total organic carbon content of the peat unit ranged from 6.9 to 32.6 percent and averaged 18 percent in 15 sediment samples (Olsen and others, 1997). The mineralogy of the lower clayey unit of the wetland sediment consists of major amounts of quartz and minor or trace amounts of mica, feldspars, kaolinite, and siderite. The total organic carbon content in four samples from this lower unit averaged about 1 percent.

Head Distributions and Flow Directions

Shallow flow directions in the aquifer along sections A-A' and C-C' are laterally westward toward the creek channel and vertically upward through the wetland and channel sediments (figs. 9 to 12). Vertically upward flow seemed predominant in the wetland sediments themselves. Although only a limited number of piezometers were successfully installed near the bottom of the aquifer, flow deep in the aquifer also seemed to be predominantly westward and upward. Tidal influences and changes in recharge conditions, however, cause some reversals in flow directions and add to the complexity of the hydrology.

The head distributions along section A-A' at low and high tides from synoptic measurements on May 2, 1996 are shown on figures 9 and 10. At low tide, ground-water flow is upward from the aquifer to the wetland sediments and creek channel at all sites in the wetland. At high tide, however, flow is downward from the creek channel into the wetland sediments. Localized downward flow in the wetland sediments was also seen at high tide at other sites along this section.

Along section C-C ' at low tide, head distributions showed that ground-water flow was entirely vertically upward over almost the entire section (fig. 11), although a hinge line [a line that separates the recharge and discharge areas (Freeze and Cherry, 1979, p. 194)] may exist near the eastern end of the section. This low-tide regime, therefore, is characterized by both a discharge zone over the entire wetland area and discharge of ground water directly into West Branch Canal Creek. Earlier that same day, synoptic measurements were made at high tide (fig. 12) when the stage in the creek was approximately 2 ft higher than at low tide. The result was a reversal in head gradients near the West Branch Canal Creek with a concomitant change in flow directions. At high tide, creek water recharges the aquifer, and ground-water discharge is concentrated at a point about 30 to 50 ft east of the West Branch Canal Creek (near sites WB-36 and WB-35 in fig. 12). This contrasts with head distributions along section A-A', where water flowing westward in the aquifer discharges on both sides of the creek at low and high tides (figs. 9 and 10).

The effect of cyclic tidal fluctuations is twofold along section C-C '. One, there is virtually no net discharge of ground water to the West Branch Canal Creek at this location. The flux from the stream and into the ground-water-flow system at high tide is balanced by a flux back out of the ground-water system and into the stream at low tide. Secondly, there is a concentrated and higher than expected discharge to the wetland sediments some 30 to 50 ft from the creek. These changing flow conditions along section C-C' obviously can greatly affect the distribution and transport of contaminants, as discussed later. Along both sections, reversals in flow directions and infiltration of surface water, which generally does not contain detectable concentrations of VOC's (Lorah and Clark, 1996, p. 173), also could increase the effects of dispersion and dilution and increase residence times of ground-water contaminants in the wetland sediments.

The response to tidal surface-water fluctuations varied at different piezometers,

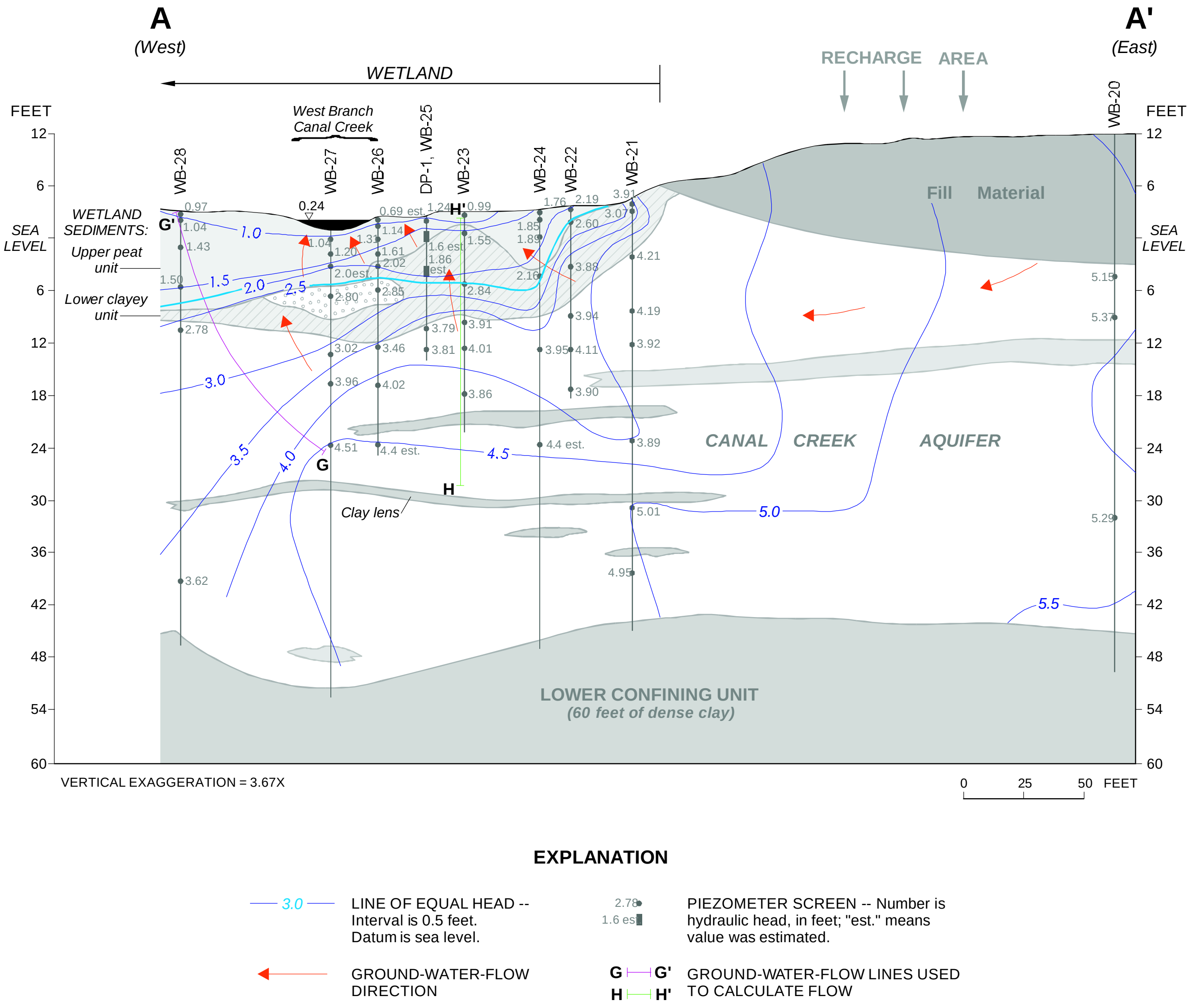


Figure 9. Section A-A' showing head distributions and ground-water-flow directions at low tide, May 2, 1996.

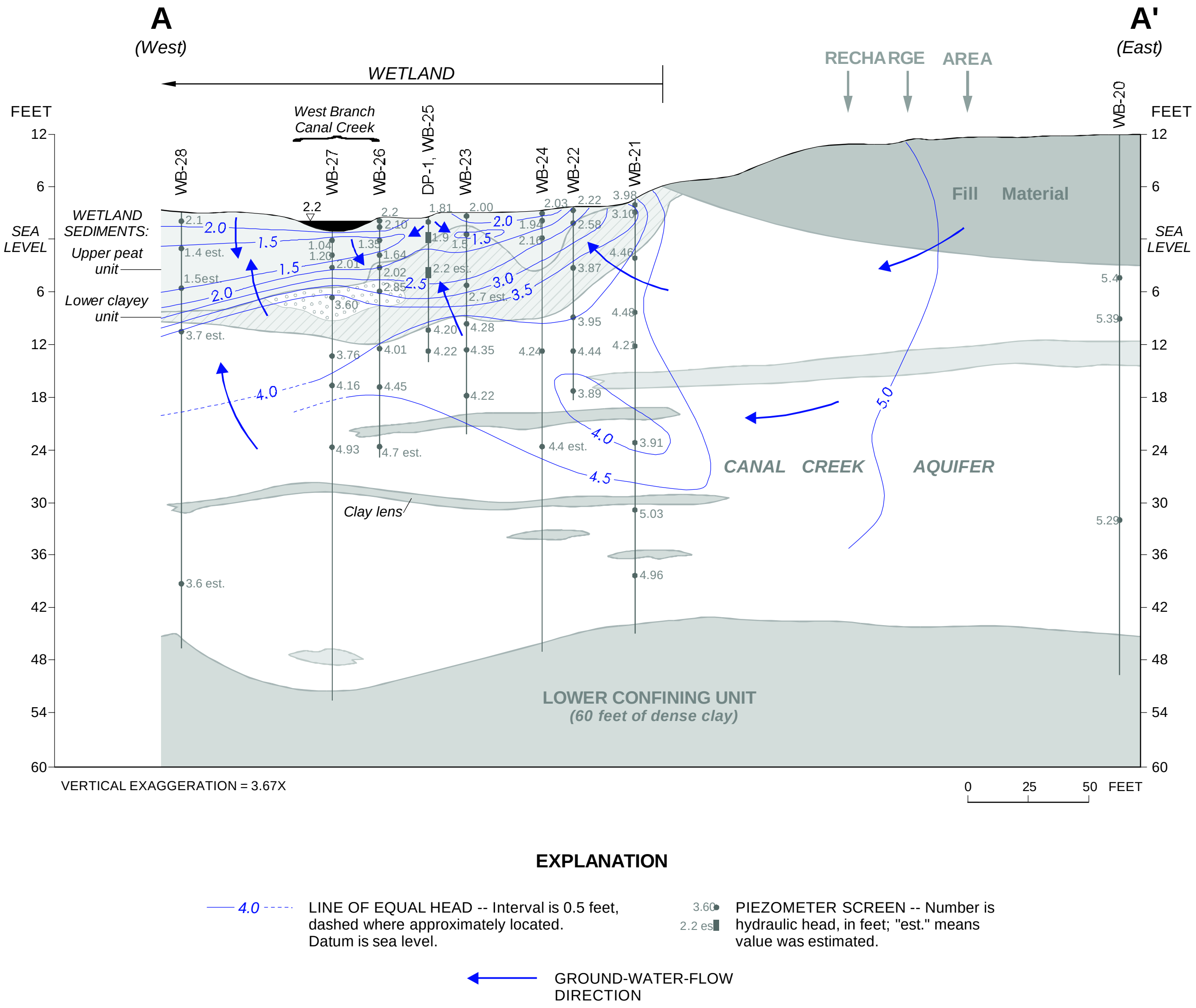
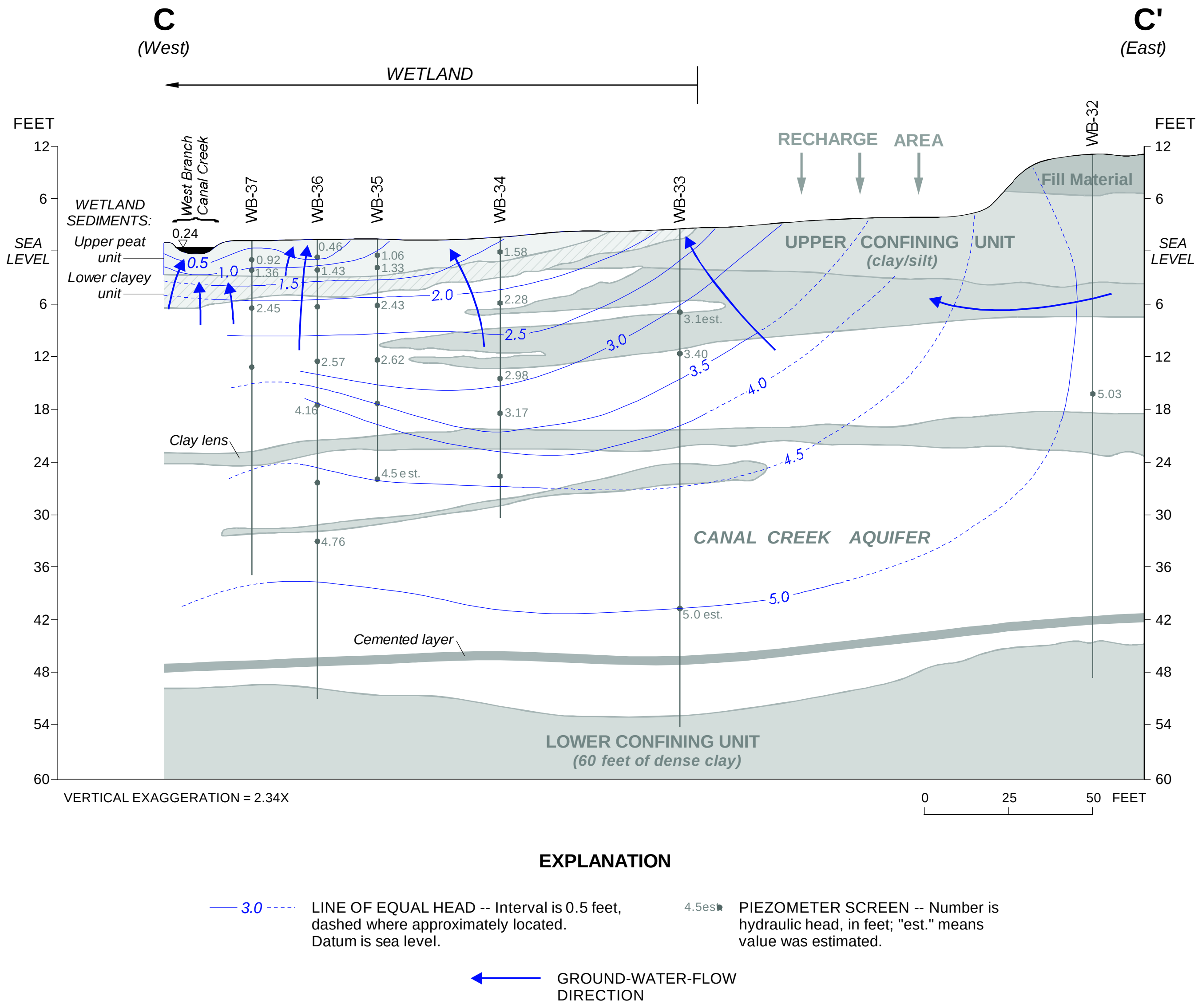


Figure 10. Section A-A' showing head distributions and ground-water-flow directions at high tide, May 2, 1996.



EXPLANATION

3.0 LINE OF EQUAL HEAD -- Interval is 0.5 feet, dashed where approximately located. Datum is sea level.

4.5est● PIEZOMETER SCREEN -- Number is hydraulic head, in feet; "est." means value was estimated.

← GROUND-WATER-FLOW DIRECTION

Figure 11. Section C-C' showing head distributions and ground-water-flow directions at low tide, May 2, 1996.

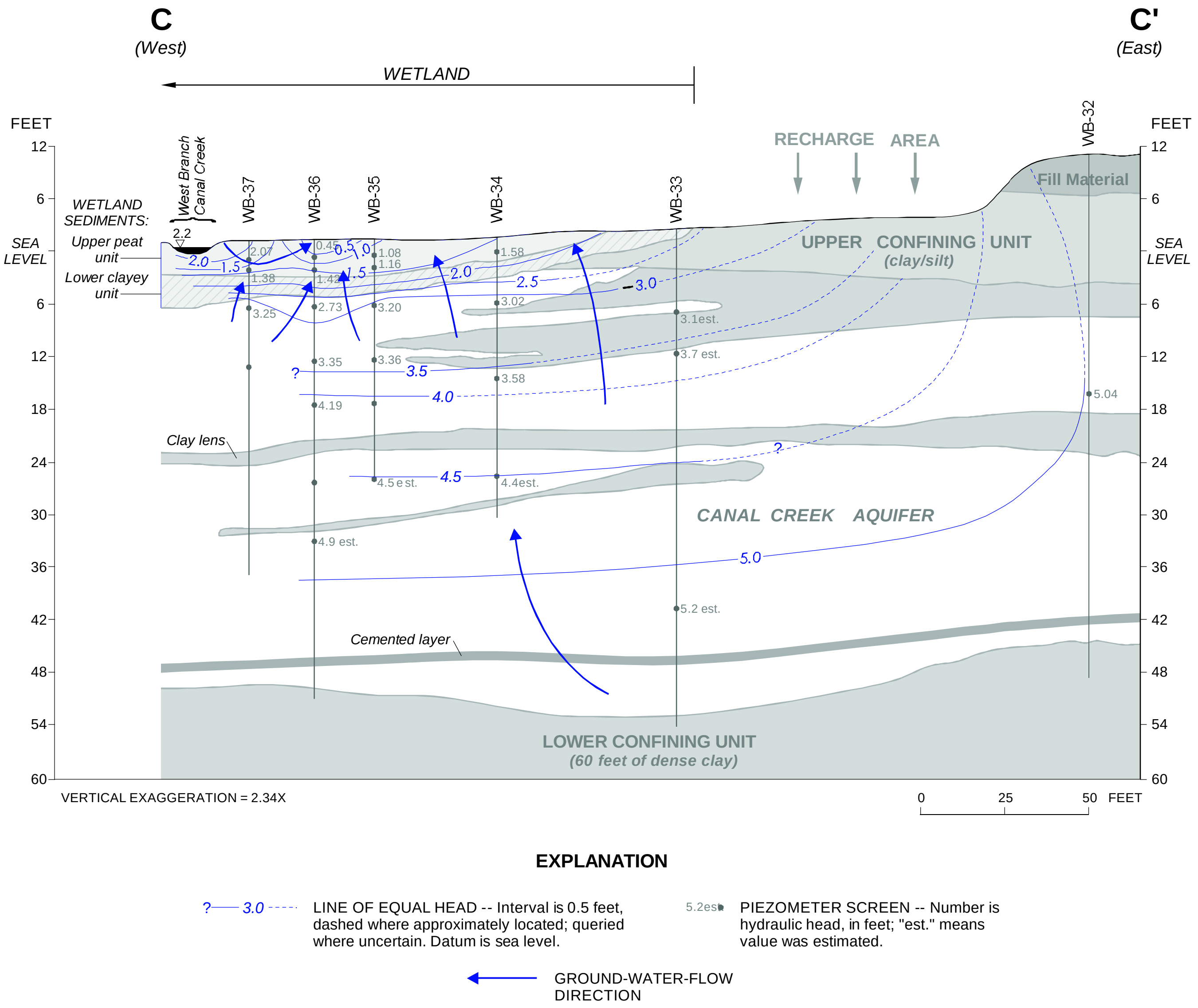


Figure 12. Section C-C' showing head distributions and ground-water-flow directions at high tide, May 2, 1996.

depending on hydraulic conductivity of the sediments and the lateral distance from the creek (figs. 7 and 8). Tidal fluctuations were evident in water-level measurements from most of the piezometers screened in the aquifer (figs. 7 and 8). The tidal fluctuations in water levels in the aquifer were generally greater than those in the wetland sediments because of the greater hydraulic conductivity of the aquifer sediments. For example, figure 13 shows hydrographs for WB-37C.1, which is a piezometer screened in the aquifer at a depth of 6.3 to 7.3 ft below land surface, and for WB-37B.1, which is screened in the upper peat unit at the same site at a depth of 2.0 to 3.0 ft below land surface. The tidal fluctuations are amplified in WB-37C.1 compared to WB-37B.1. The magnitude of the tidal response in the aquifer generally decreased with depth and lateral distance from the creek. In the wetland sediments, tidal fluctuations were most evident in a few shallow piezometers screened near the top of the upper peat unit (figs. 7, 8, and 13). Here, in piezometers such as WB-37B.1, the tidal response indicates that water is flushing back and forth in the sediments in concert with the tide (fig. 13). Other piezometers that are screened in the upper peat unit and located near the creek bank, such as DP-1A (fig. 7), did not show a response to tidal fluctuations in creek stage, most likely because they are screened in more clayey sediments. Thus, the variability in the response to tidal fluctuations reflects the heterogeneity of the wetland sediments. None of the piezometers screened in the lower clayey unit of the wetland sediments responded to tidal fluctuations in the creek, indicating that this unit generally had a lower hydraulic conductivity than the peat or aquifer sediments.

Although head distributions generally did not vary substantially on a seasonal basis, a change in

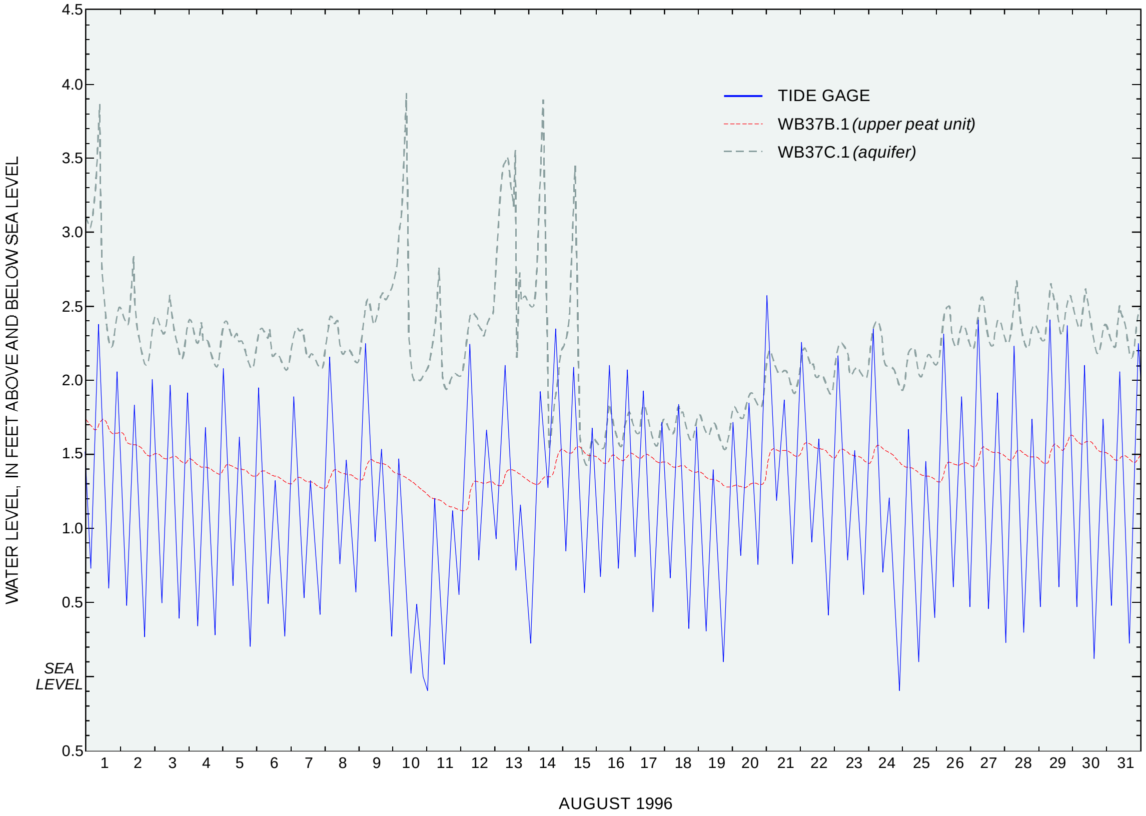


Figure 13. Hydrograph showing the response of water levels in piezometers to tidal fluctuations in the stage of West Branch Canal Creek.

recharge conditions between 1995 and 1996 did affect the flow system in the study area. Precipitation at the Aberdeen weather station for 1995 was 41.23 in. (National Oceanic and Atmospheric Administration, 1996, p. 3), which is close to the average precipitation of 42 in/yr for the Canal Creek area (Lorah and Clark, 1996, p. 9). Precipitation for 1996, however, was about one-third above normal (56.22 in.). Along section A-A', some flow in the Canal Creek aquifer upgradient of the wetland boundary (between sites WB-20 and WB-21) was to the east, away from the wetland and creek in April 1995, rather than entirely toward the wetland as in May 1996 when high recharge conditions existed (figs. 9, 10, and 14). Lorah and Clark (1996, p. 16) indicate that a ground-water saddle exists along the West Branch Canal Creek. In addition, a small ground-water divide exists in the vicinity of the east end of section A-A' (Lorah and Clark, 1996, p. 57). The configuration of this divide is likely to change as the amount of recharge changes, causing the principal direction of ground-water flow to change from westward toward the West Branch Canal Creek to southward or southwestward towards the confluence of the East and West Branches of Canal Creek. Northward flow is also possible, which would result in discharge to a more upstream segment of West Branch Canal Creek. Either of these scenarios could cause the change in the flow pattern observed along section A-A' from 1995 to 1996.

The synoptic measurements made during 1995-96 indicate that the flow pattern shown in figure 14 persisted throughout most of 1995, while the flow pattern shown in figures 9 and 10 persisted throughout most of 1996. Thus, during periods of higher than normal precipitation, heads in the Canal Creek aquifer to the east of the wetland boundary are built up sufficiently to develop a flow system that is predominantly westward, as shown in figures 9 and 10, creating conditions of maximum discharge into the wetland along section A-A'. As heads decline during periods of lower recharge, less ground-water flux through section A-A' may occur (fig. 14).

Hydraulic Conductivities

Horizontal hydraulic conductivities that were calculated for the upper and lower units of the wetland sediments and for the sediments of the Canal Creek aquifer underlying the West Branch study area are shown in table 3. Horizontal hydraulic conductivity is several orders of magnitude greater in the Canal Creek aquifer than in the wetland sediments, as indicated by the relative tidal fluctuations in water levels in the different units (figs. 7, 8, and 13). The median of 14 values of hydraulic conductivity estimated for the aquifer is 2 ft/d, which is almost three orders of magnitude greater than the median value for the wetland sediments. The estimated hydraulic conductivities for the Canal Creek aquifer in the West Branch area are typical of an aquifer composed of fine sand (Fetter, 1994, table 4.6) with stringers of both coarse, gravelly material and finer silt and clay. A median value of 23 ft/d was measured for the aquifer from slug tests in wells located throughout the Canal Creek area (Lorah and Clark, 1996, p. 202), indicating that the sands of the Canal Creek aquifer are somewhat finer-grained locally within the West Branch area.

For the upper peat unit of the wetland sediments, the calculated values for hydraulic conductivity ranged from 0.0003 to 0.04 ft/d and had a median of 0.004 ft/d for 15 values. The two hydraulic conductivity values that were calculated for the lower clayey unit of the wetland sediment were 0.0008 and 0.04 ft/d, which differ by more than two orders of magnitude. The lower value is probably more representative of hydraulic conductivities within the lower clayey unit, because the head distributions and tidal responses indicate that hydraulic conductivities probably are lower in the lower clayey unit than in the upper peat unit. However, hydraulic conductivity is quite variable in both units. The paleochannel deposit at site WB-27 in section A-A' had a hydraulic conductivity of 120 ft/d, which is greater than values estimated for the Canal Creek aquifer or wetland sediments.

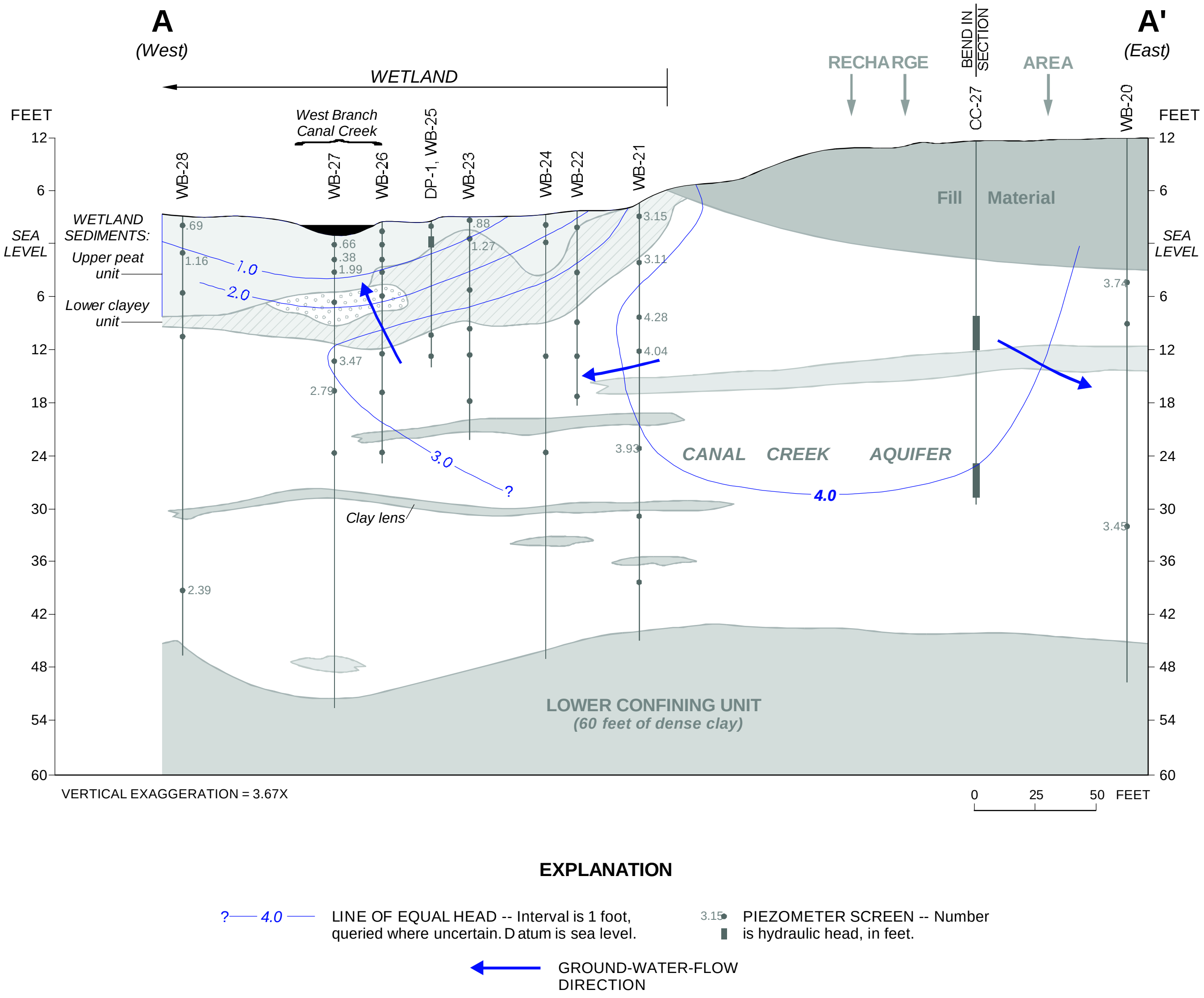


Figure 14. Section A-A' showing head distributions and ground-water-flow directions at high tide, April 5, 1995, when recharge to the aquifer was low.

Table 3. *Horizontal hydraulic conductivities in aquifer and wetland sediments in the West Branch study area, Aberdeen Proving Ground, Maryland*

[K, horizontal hydraulic conductivity in feet per day; aquifer, Canal Creek aquifer; upper, upper peat unit of the wetland sediments; lower, lower clayey unit of the wetland sediments. The sediment sample number indicates the piezometer and, in paraentheses, depth in feet below land surface at which sample was collected]

Piezometer no.	Sediment sample no.	Lithologic unit	K from slug test [1]	K from sieve analysis [2]	K from tidal analysis [3]
	WB-21 (8-10)	aquifer		73	
WB-21C		aquifer	10		
WB-22B		lower	.04		
WB-24B		upper	.4		
WB-24D		aquifer			6
WB-26A		upper	.05		
WB-26B		upper	.001		
WB-26C		upper	.006		
WB-26D		lower	.0008		
	WB-27(8-10)	paleochannel		120	
WB-27E		aquifer			.2
WB-28A		upper	.01		
WB-28B		upper	.0009		
WB-28C		upper	.0003		
WB-34A		upper	.0003		
WB-35A		upper	.003		
WB-35B		upper	.06		
WB-35C	WB-35 (7-10)	aquifer	7	.7	.9
WB-35D	WB-35 (10-12)	aquifer	.01	13	
WB-35E		aquifer	2		
WB-36B		upper	.0007		
	WB36 (10-12)	aquifer		77	
WB-36E		aquifer	2		
WB-37A		upper	.04		
WB-37B		upper	.0005		.01
WB-37C		aquifer			.06
DP-1A		upper			.09
DP-4B		aquifer			.2

[1] Bouwer-Rice method (Fetter, 1994, p. 251-256).

[2] Hazen method (Fetter, 1994, p. 99).

[3] Ferris method (Tenbus and Fleck, 1996, p. 16-17).

Flow Velocities and Discharge Rates

The average linear flow velocities in the aquifer and wetland sediments and the specific discharge of ground water to the wetland surface were estimated for sections A-A' and C-C', using the head distributions measured at low tide on May 2, 1996 (figs. 9 to 12). To estimate total discharge (Q_t, equation 6) to the wetland surface, flow nets also were constructed for sections A-A' and C-C' for the same date. Section A-A' was less amenable to flow-net analysis than section C-C' because of the sharp changes in head gradients. The total discharges estimated for the two sections, however, were approximately equal, giving some assurance of the validity of this approach. The flow net constructed for section C-C' is shown in figure 15 as an example. Although the flow net for section A-A' is not shown, the flow lines G-G ' and H-H' that were used in the velocity and discharge calculations are shown in figure 9. Flow line F-F ' was used in the calculations for section C-C ' (fig. 15).

Because the flow under this part of section C-C' is vertical, the vertical component of hydraulic conductivity was calculated using equation 3. Flow line F-F' was divided into 13 increments with b_i varying from 0.6 to 6.7 ft and K_i varying from 0.001 to 75 ft/d. The effective vertical hydraulic conductivity, K_z, was 0.02 ft/d, and the length, l ,was 31.8 ft. Substituting these values into equations 2 and 4, the specific discharge, q, at the wetland surface is 0.0025 ft/d for a unit area of 1 ft^2. This is equivalent to 11 in/yr.

To calculate the average linear velocity (v) along the entire flow line F-F', an estimated effective porosity of 0.3 was used, which is typical of fine sand with interfingers of clay and gravel (Fetter, 1994, table 4.3). Substituting in equation 5, the average linear velocity is about 3 ft/yr along the entire flow line. The same calculations were made for the part of flow line F-F ' that includes only the wetland sediments, which is the upper 5.5 ft of flowpath F-F ', and only the aquifer. The calculations for the part of flow line F-F ' that includes only the aquifer gave the same average linear velocity as calculated for the entire flow line (3 ft/yr). The low velocity estimated for the aquifer along this vertical flow line is caused by the low vertical hydraulic con-ductivity where clay and silt layers are present in the aquifer. If these layers can be breached along the upward flowpaths, the flow velocities in the aquifer could be more than an order of magnitude higher than 3 ft/yr.

The average linear velocity of ground water in the wetlands sediments is estimated to be only slightly lower than the velocity in the aquifer. To calculate the flow velocity in the wetland sediments, the average effective porosity for the upper peat unit and lower clayey unit of the wetland sediment was estimated to be 0.4. This is at the low end of the range of porosity values that are typical for silts and clays with less than 20 to 35 percent organic carbon (Mitsch and Gosselink, 1986, p. 91; Fetter, 1994, table 4.3). This low number was chosen because effective porosity typically is lower than actual porosity, which can include unconnected spaces between sediment particles. Using the effective porosity of 0.4 and an average vertical hydraulic conductivity (K_z) of 0.007 ft/d, the average linear velocity in the wetland sediments is about 2.3 ft/yr along flow line F-F'. Although the vertical hydraulic conductivity is lower in the wetland sediments than in the aquifer, the increase in the vertical head gradient as the wetland sediments are reached results in similar flow velocity estimates for the wetland and aquifer. Preferential flow along macropores, such as along root channels, could cause higher flow velocity in the wetlands than estimated above.

Along section A-A', similar calculations were made along flowpaths G-G ' and H-H'. Flowpath G-G' represents vertical flux upward from under the West Branch Canal Creek to the wetland on the western bank of the creek, covering a distance of about 32 ft. This path crosses 11 ft of the upper peat unit and 2 ft of the lower clayey unit of the wetland sediments. For flow line G-G', the average vertical hydraulic conductivity (K_z) was 0.0064 ft/d; the specific discharge (q) was 0.0007 ft/d, or about 3 in/yr; and the average linear velocity (v) was 0.0020 ft/d, or about 0.7 ft/yr. Along flowpath H-H', water discharges vertically through 1.5 ft of the upper peat unit and 6.5 ft of the lower clayey unit of the wetland

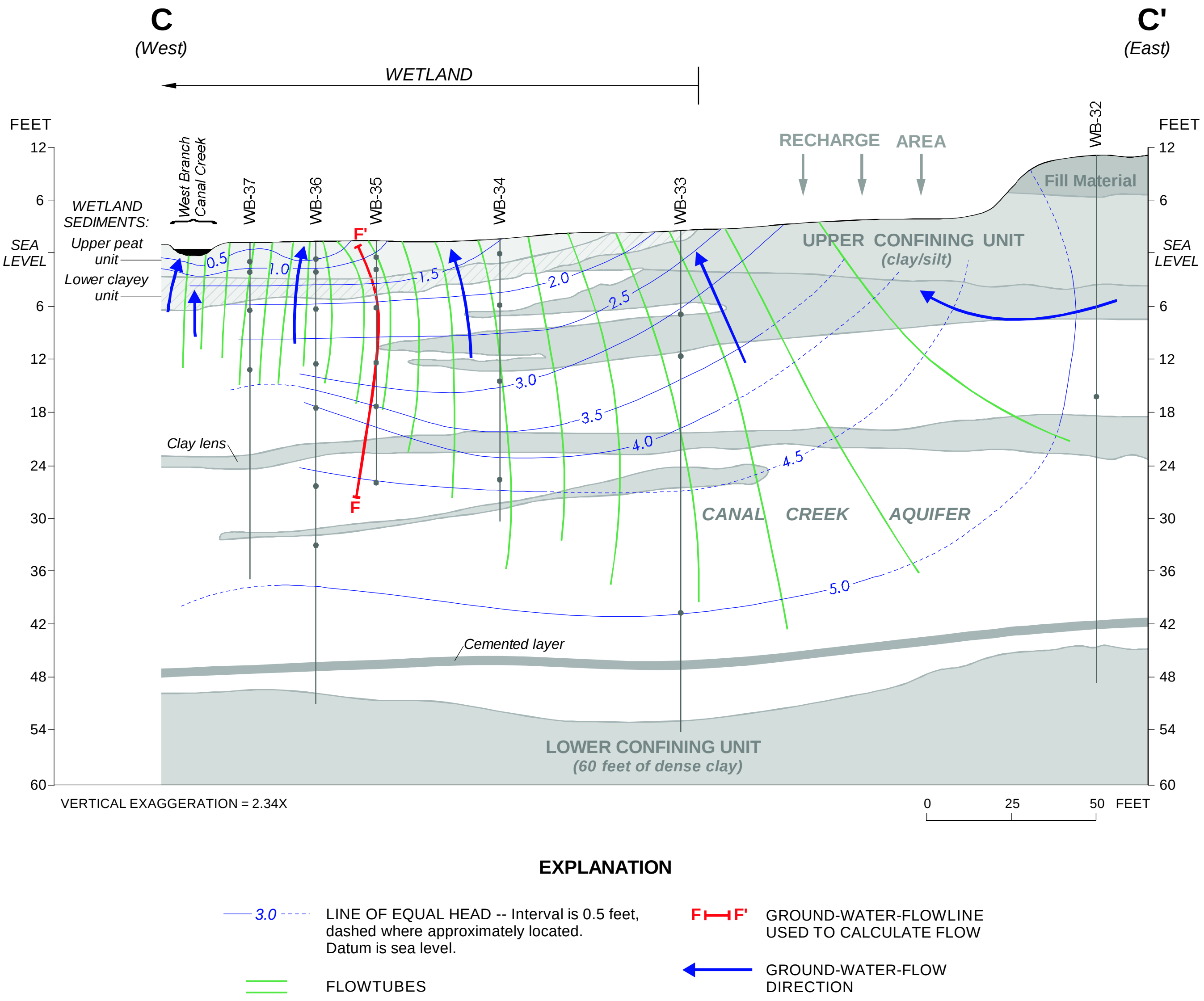


Figure 15. Flow net for section C-C' at low tide, May 2, 1996.

sediments. For this flowpath, the average vertical hydraulic conductivity was 0.003 ft/d; the specific discharge was 0.0019 ft/d, or about 8 in/yr; and the average linear velocity was 0.006 ft/d, or 2.3 ft/yr.

For the tube that includes stream path F-F ' in the flow net for section C-C ', the total discharge to the wetland surface is 0.0125 ft^2/d per unit aquifer width. The flow net encompasses 18 tubes from the eastern wetland boundary to the creek; therefore, the total discharge along a 1-ft-wide strip of wetland surface is 0.225 ft^2/d. For section A-A', flow-net analysis indicates that the total discharge along a 1-ft-wide strip of wetland area extending from the eastern wetland boundary to the creek is in the range of 0.13 to 0.25 ft^2/d. The estimates of total discharge to the wetland surface, therefore, were in the same range for the two sections.

Distribution of Volatile Organic Compounds

The distribution of VOC's along the two transects through the wetland (fig. 3) is discussed in this section, focusing on the total concentrations of VOC's and the major parent contaminants observed. VOC's that were detected infrequently, at a limited number of sites, or in relatively low concentrations are not discussed unless they are a possible degradation product of the primary contaminants. Possible degradation products will be discussed in the section Biodegradation and Abiotic Degradation.

Ground water at the background site, WB-19 (fig. 3), generally had undetectable concentrations of VOC's throughout the wetland sediment and Canal Creek aquifer, although there were some sporadic detections of TCE, PCA, CF, toluene and MTBE (methyl tert-butyl ether) (Olsen and others, 1997). During the comprehensive sampling in June-October 1995, the highest contaminant concentration detected at the back-ground site was 1.1 µg/L of MTBE in the shallowest sampling point in the wetland sediment (WB-19A). During the four seasonal sampling periods, one of the piezometers screened in the wetland sediment (WB-19B) and one screened in the aquifer (WB-19E) were monitored. The only VOC's detected in the background piezometers during these four sampling periods were PCA (0.9 µg/L) in WB-19B in August 1996 and PCA (1.2 to 3.0 µg/L in triplicate samples) and TCE (less than 0.2 to 0.6 µg/L in triplicate samples) in WB-19E in March-April 1996 (Olsen and others, 1997).

Section A-A'

Along section A-A', total concentrations of VOC's were highest in the aquifer upgradient of the eastern edge of the wetland (fig. 16). Total concentrations of VOC's were about 5,000 µg/L in samples from the shallow well at site CC-27 (CC-27A), which is located near a suspected source from a past sewerline discharge point (fig. 3). This concentration is an order of magnitude higher than concentrations elsewhere along the eastern side of the creek, including in the deeper well at site CC-27. Downward transport of the contaminants in the aquifer could have been partly impeded by the clayey silt layer located below the screen in CC-27A. Total concentrations of VOC's also were extremely high at the deepest piezometer at site WB-28 (WB-28F), which is located on the western side of the creek channel. Here, the total concentration of VOC's was nearly as high as observed at CC-27A (fig. 16). The major contaminants differed, however, in these two sampling points (figs. 17 to 19), indicating that they were derived from different sources. Upgradient of CC-27, relatively high concentrations of VOC's were observed in the deepest sampling point at site WB-20. It is likely that these contaminants also are part of a plume from a source other than the sewerline discharge point. The VOC plume in the aquifer was found to extend about 1,000 ft upgradient of site CC-27 during the previous investigation in the Canal Creek area (fig. 2), and multiple possible contaminant sources were identified (Lorah and Clark, 1996, p. 145-149).

Moving downgradient in the aquifer from site CC-27, concentrations of VOC's remained highest in the shallow region of the aquifer, as would be expected because of the upward flow gradient in the aquifer within the wetland area (figs. 9 and 10). Total concentrations of VOC's were greater than 500 µg/L in a thin zone that extends to the

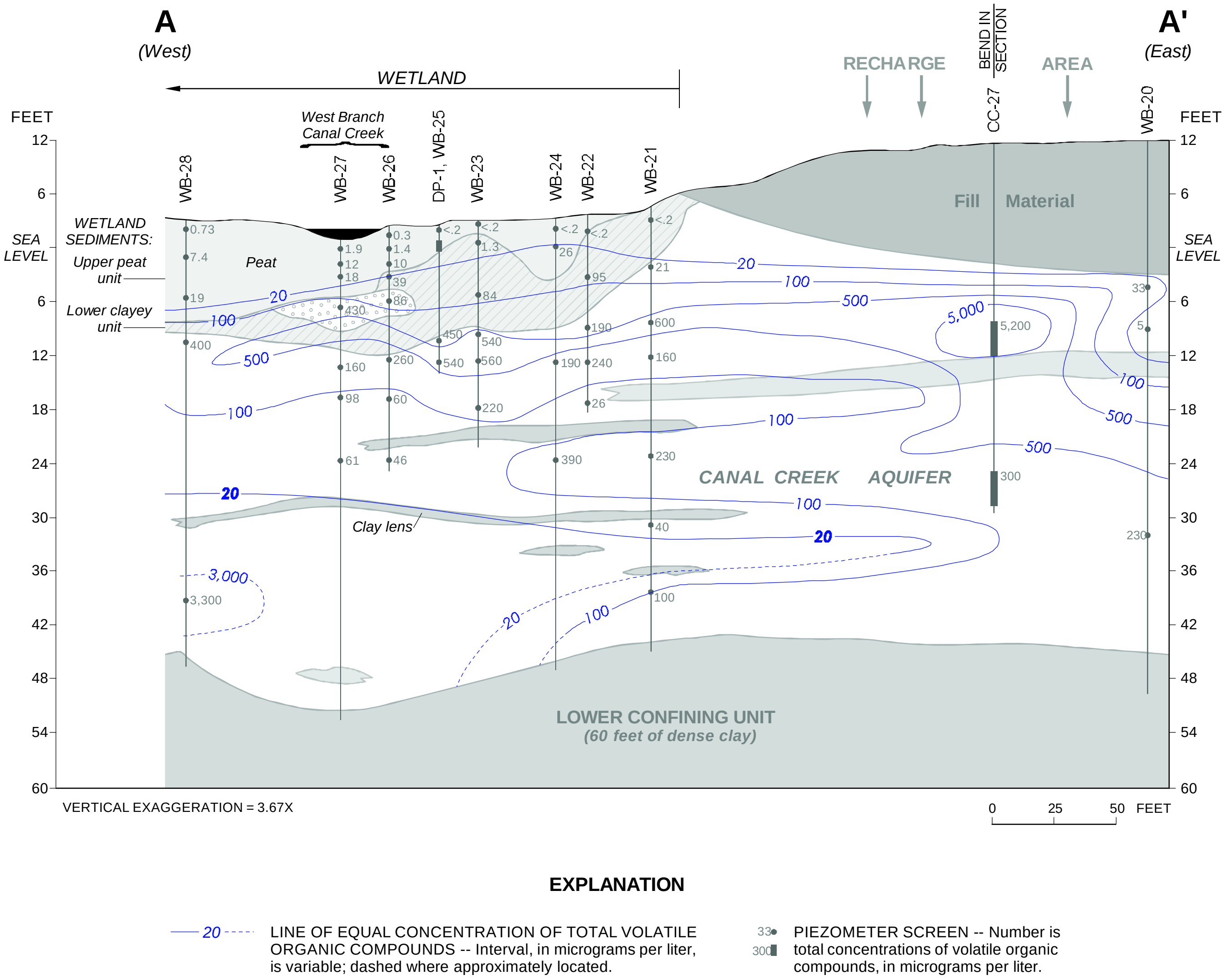


Figure 16. Section A-A' showing the distribution of total concentrations of volatile organic compounds in ground water, June-October 1995.

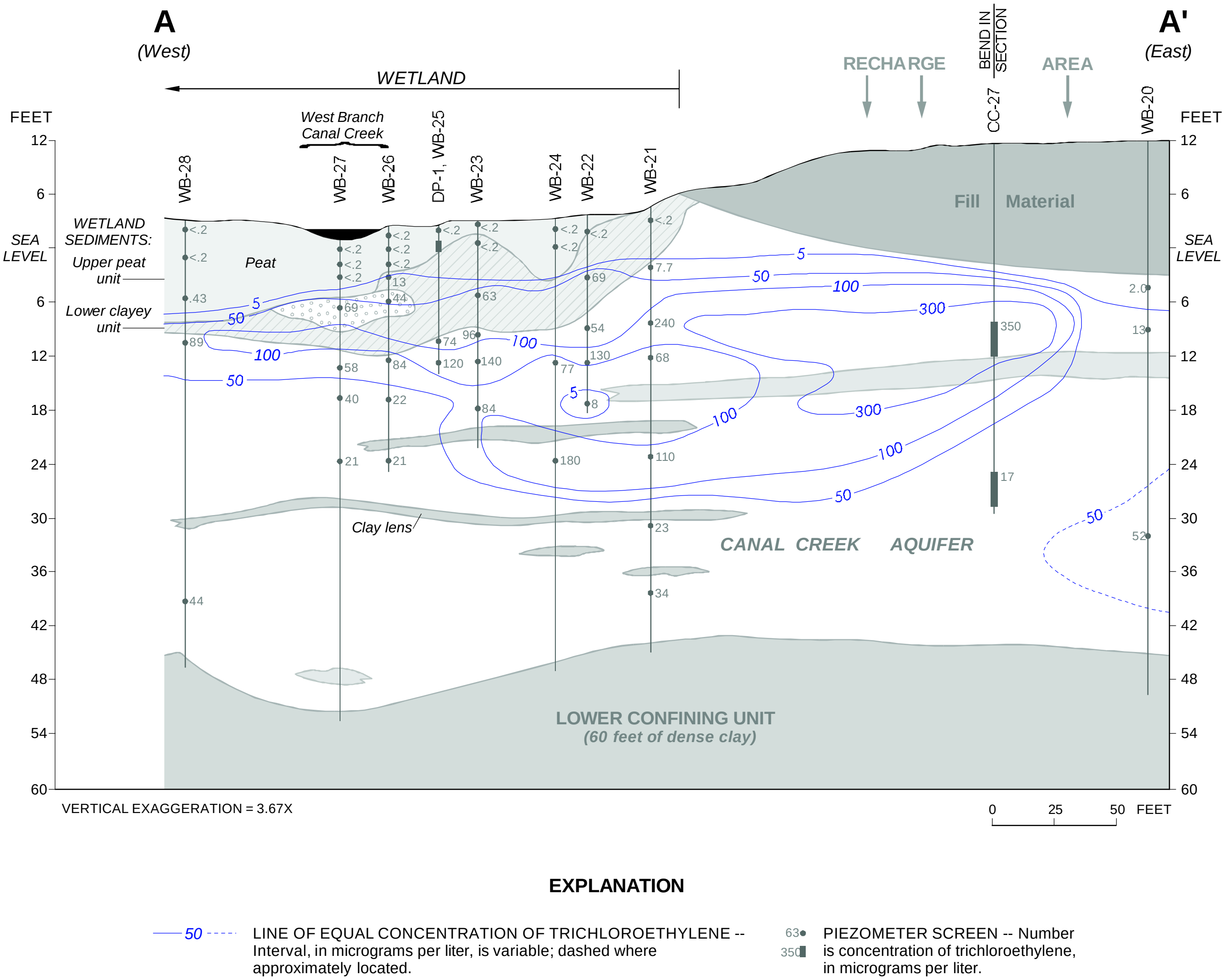
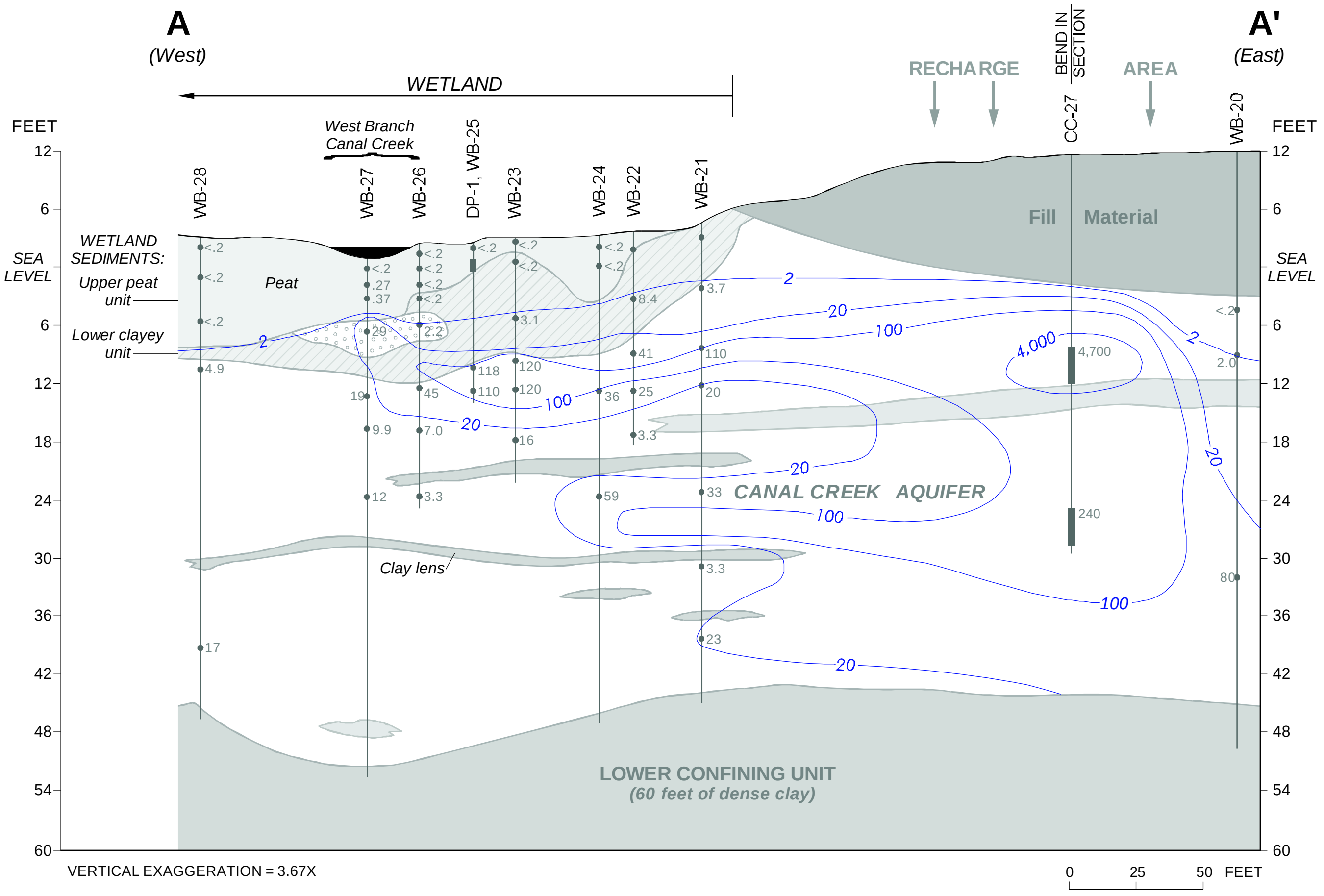


Figure 17. Section A-A' showing the distribution of trichloroethylene (TCE) in ground water, June-October 1995.



EXPLANATION

—— 20 ——	LINE OF EQUAL CONCENTRATION OF 1,1,2,2-TETRACHLOROETHANE -- Interval, in micrograms per liter, is variable.
80● 240▮	PIEZOMETER SCREEN -- Number is concentration of 1,1,2,2-tetrachloroethane, in micrograms per liter.

Figure 18. Section A-A' showing the distribution of 1,1,2,2-tetrachloroethane (PCA) in ground water, June-October 1995.

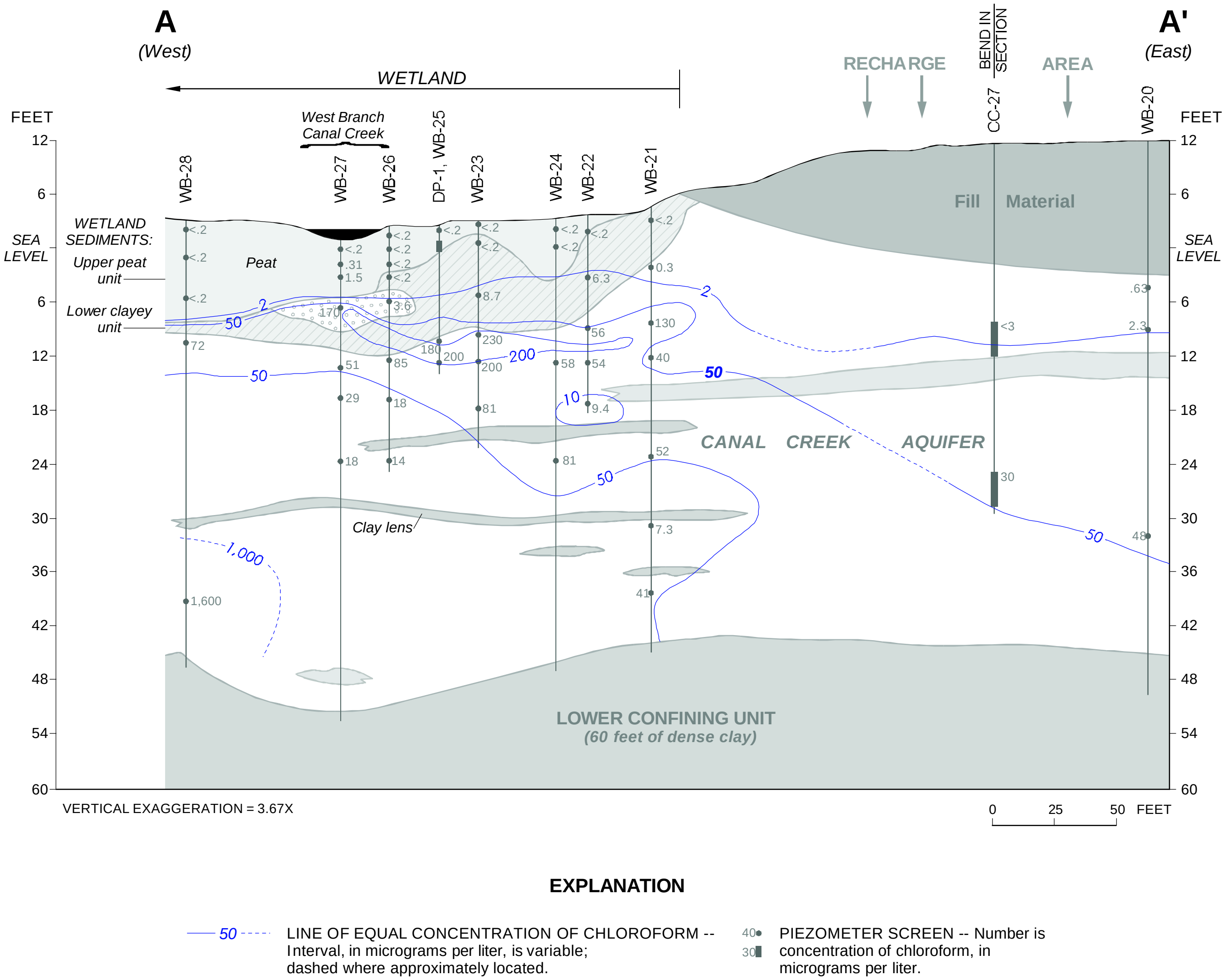


Figure 19. Section A-A' showing the distribution of chloroform (CF) in ground water, June-October 1995.

western side of the creek channel and lies directly beneath the wetland sediments. Some contaminated ground water in the aquifer, therefore, flows beneath the creek and discharges to wetland sediments on the western side. Total concentrations of VOC's in the water decreased substantially, however, along the upward direction of flow through the overlying wetland sediments. Concentrations of VOC's were about 100 µg/L in the lower clayey unit of the wetland sediments but decreased to about 20 µg/L at the base of the upper peat unit. Concentrations were below 2 µg/L within 1 to 3 ft below land surface (fig. 16). These upward decreasing concentrations indicate that natural attenuation processes are removing VOC's from the ground water in the wetland sediment.

The major parent VOC's observed in the aquifer along A-A' were TCE, PCA, CT, and CF. TCE and PCA had similar distributions, occurring in the highest concentrations at CC-27A and spreading downgradient predominantly in two fingers that remain shallow in the aquifer (figs. 17 and 18). Although concentrations of PCA (about 4,000 µg/L) were an order of magnitude higher than TCE (about 300 µg/L) near the suspected source by site CC-27, their concentrations are similar downgradient in the aquifer along A-A'. Concentrations of TCE and PCA were each in the range of 100 to 200 µg/L beneath the wetland sediments.

The distributions of CF and CT were different than those observed for TCE and PCA (figs. 17 to 19). The distribution of CF is shown in figure 19 as an example; concentrations of CT were slightly lower than CF but showed the same distribution. Because CT and CF were known to be used and disposed of together at a nearby CN (chloroacetophenone) manufacturing plant (Lorah and Clark, 1996, p. 148), the close association of these compounds is not surprising. The highest concentrations of CF and CT were observed in the aquifer downgradient within the wetland area, rather than upgradient of the wetland. The maximum concentrations of CF and CT (about 1,600 and 560 µg/L, respectively) occurred in the deepest sampling point at site WB-28 (WB-28F). The source of the anomalously high concentrations at WB-28F, which were confirmed on subsequent sampling events, is unknown. It is possible that solvents in their raw, undissolved form were discharged through sewerlines directly to the creek channel and caused a pool of DNAPL's at the base of the aquifer. Because deep piezometers that were installed at sites WB-27 and WB-26 were broken, the extent of contamination at the bottom of the aquifer under the creek channel could not be defined (fig. 19). In addition to piezometer WB-28F, CF and CT concentrations were relatively high in the old channel deposit of sand and gravel at site WB-27 and in a thin zone in the aquifer directly beneath the wetland sediments. Concentrations of CF and CT were generally less than 2 µg/L in the wetland sediments, again indicating that the VOC's are naturally attenuated as ground water discharges upward.

Section C-C'

The total concentrations of VOC's and the distribution of individual contaminants differed along section C-C' compared to A-A'. Higher total concentrations of VOC's extended further downgradient in the shallow region of the aquifer and upward into the wetland sediments along section C-C' than observed along section A-A' (figs. 16 and 20). Total concentrations of VOC's in the aquifer were as high as 2,100 µg/L at site WB-32, which is upgradient of the wetland, and at site WB-33, which is at the eastern edge of the wetland area. The plume has an upward trend into the wetland sediments, and the maximum concentrations in the wetland sediments were observed at site WB-35. In contrast to section A-A', where concentrations of total VOC's were nearly 500 µg/L in the shallow aquifer on the western side of the creek (fig. 16), the contaminant plume does not appear to reach the creek channel or the western side of the creek along section C-C' (fig. 20). Concentrations of total VOC's were undetectable or relatively low (about 50 µg/L) in ground water adjacent to the creek channel (site WB-37 in fig. 20). The contaminant distributions, therefore, agreed with the head distributions, which indicated that the area around sites WB-35 and WB-36 was the major discharge area of the aquifer along this section (fig. 20).

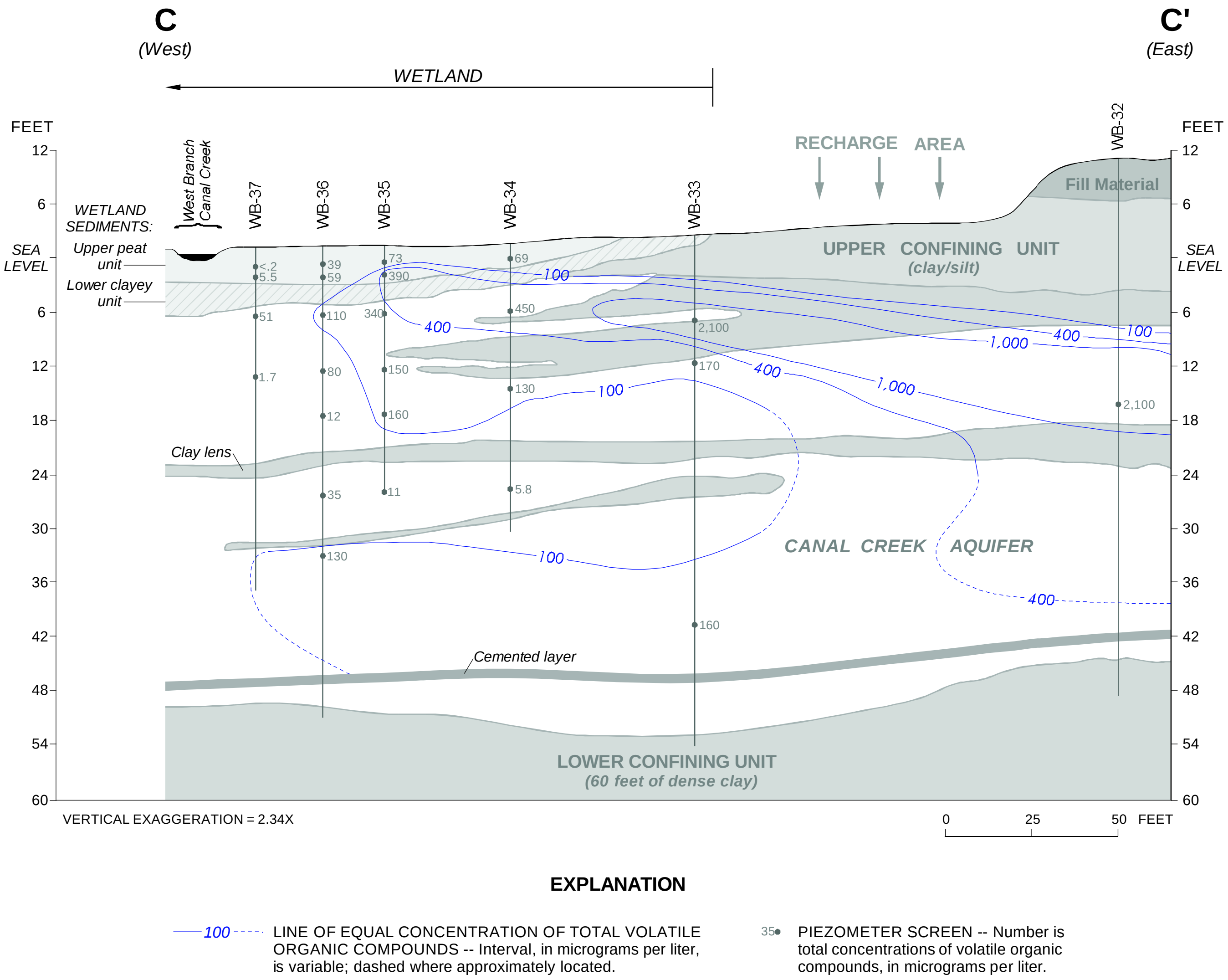


Figure 20. Section C-C' showing the distribution of total concentrations of volatile organic compounds in ground water, June-October 1995.

Because the wetland sediments are relatively thin along section C-C', piezometers were placed only in the upper peat unit, which is 3 to 4 ft thick. At site WB-35, total concentrations of VOC's were close to 400 µg/L in the piezometer screened at the base of the upper peat unit at a depth of 2.8 to 3.3 ft below land surface (WB-35B) and then decreased to about 70µg/L in the piezometer screened at 1.5 to 2.0 ft below land surface (WB-35A). Total concentrations of VOC's in the upper peat unit also were in the range of 50 to 100µg/L at sites WB-34 and WB-36 in samples that were collected from piezometers screened at depths between 1.5 and 3.0 ft below land surface (fig. 20).

Ground-water samples collected from peepers placed at sites WB-34, WB-35, and WB-36 at various times between 1995-96, however, showed that total concentrations of VOC's generally were less than 5 µg/L within 0.5 ft below land surface (Olsen and others, 1997). Figure 21 shows the distribution of total VOC's observed in peepers placed at sites WB-35 and WB-36, where the highest concentrations were observed in the wetland sediment. Concentrations of VOC's showed an upward decreasing trend and were below detection near land surface (fig. 21). This demonstrates that natural attenuation in the wetland sediments is effective even where relatively high concentrations are discharging upward through very thin layers of wetland sediment.

PCA was the major contaminant in the ground water along section C-C', occurring at a maximum concentration of about 2,000 µg/L in the aquifer at site WB-32 and WB-33 (fig. 22). As seen along section A-A', the PCA plume was primarily in the shallow region of the aquifer. The maximum PCA concentration in water in the wetland sediment (300 µg/L) was measured in WB-35B, which is screened near the base of the upper peat unit. PCA concentrations, however, were more than two orders of magnitude lower in the water from WB-35A (fig. 22). Next to the creek channel at site WB-37, PCA was less than 0.2 µg/L, except in one piezometer screened immediately below the wetland sediment.

Unlike section A-A' where both PCA and TCE were major ground-water contaminants, TCE concentrations were much lower than PCA concentrations in the aquifer and wetland sediment along section C-C' (figs. 22 and 23). TCE concentrations were a maximum of 54 µg/L at site WB-32 and decreased to between 10 and 20µg/L in a thin plume that extends beneath the wetland sediment to site WB-35.

Concentrations of CF and CT also were lower in the ground water along section C-C' than along section A-A'. The maximum concentration of CT in the ground water along section C-C' was only 21µg/L and was observed in the deepest piezometer at site WB-33 (WB-33F), which is screened in the aquifer at a depth of 42.5 to 43.0 ft below land surface (fig. 8). The highest concentrations of CF were about 100 µg/L and were observed in WB-33F and in WB-36G, which is the only other deep piezometer along section C-C' (fig. 24). Elsewhere in the aquifer, CF concentrations generally were not greater than 10 to 30µg/L. Most of these detections were measured at various depths in the aquifer at site WB-36. Concentrations of CF in water in the wetland sediments were less than about 2 µg/L (fig. 24). Overall, the relatively high concentrations of CF deep in the aquifer compared to the shallow PCA plume indicate different sources for these contaminants, as observed along section A-A'.

Seasonal Variations

Seasonal variations in the distribution of the major VOC's might be expected from variations in ground-water heads and flow directions and in biodegradation and volatilization rates. Few substantial changes in concentrations of the major parent contaminants, however, were observed during the different sampling periods in 1995-96. Comparing data from piezometers sampled during each of four sampling periods (June-October 1995, March-April 1996, June 1996, and August 1996), median concentrations of TCE and PCA in the aquifer varied from 58 to 130 µg/L and from 94 to 110 µg/L, respectively (table 4). The seasonal variability in the median concentrations of PCA in the aquifer is less than the variability expected from sampling and analytical precision. The difference in median concentrations of TCE in the aquifer, however, was as high as 125 percent, which is substantially greater than the sampling and analytical variability. The relative

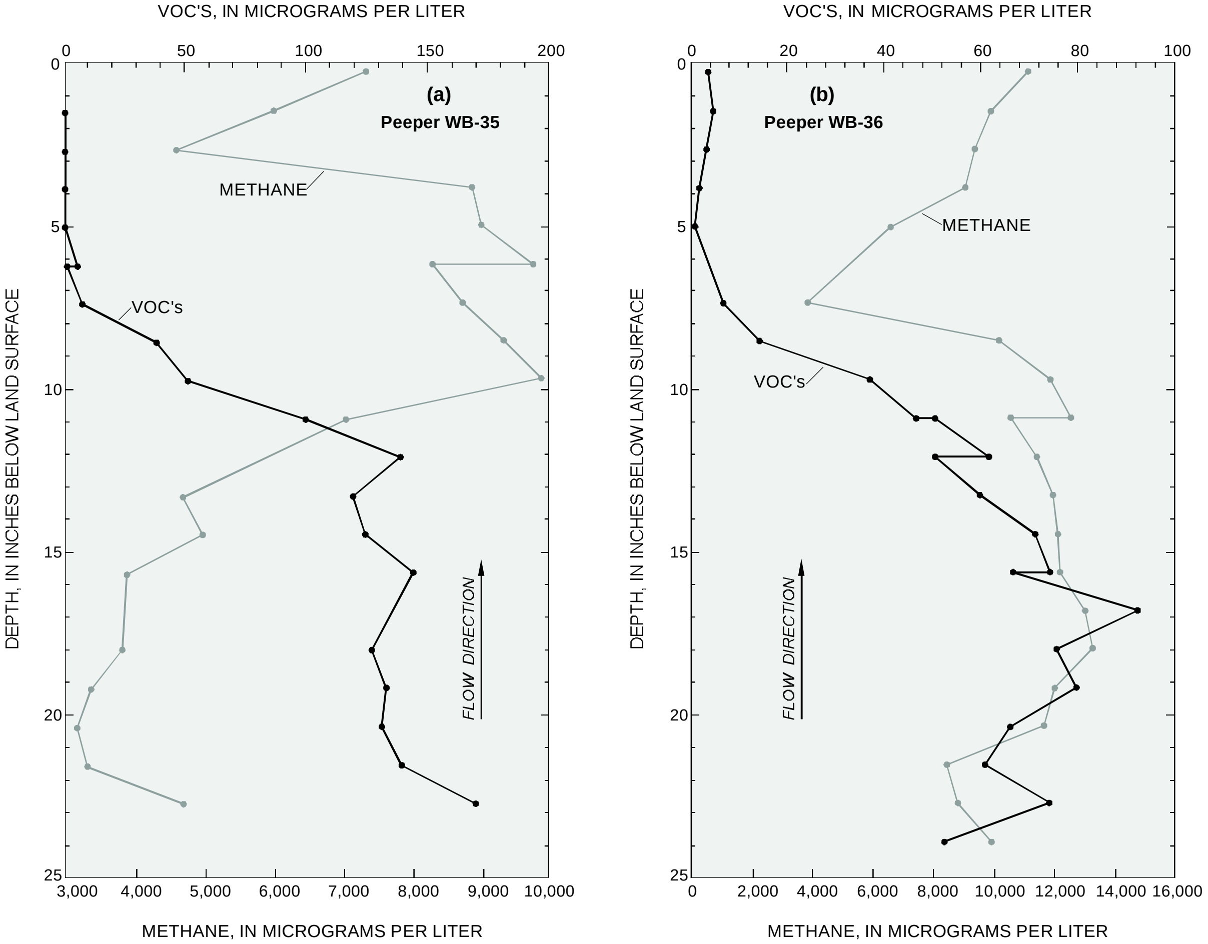


Figure 21. Vertical distribution of total concentrations of chlorinated volatile organic compounds (VOC's) and methane in peepers placed at site **(a)** WB-35 and **(b)** WB-36, June 1996.

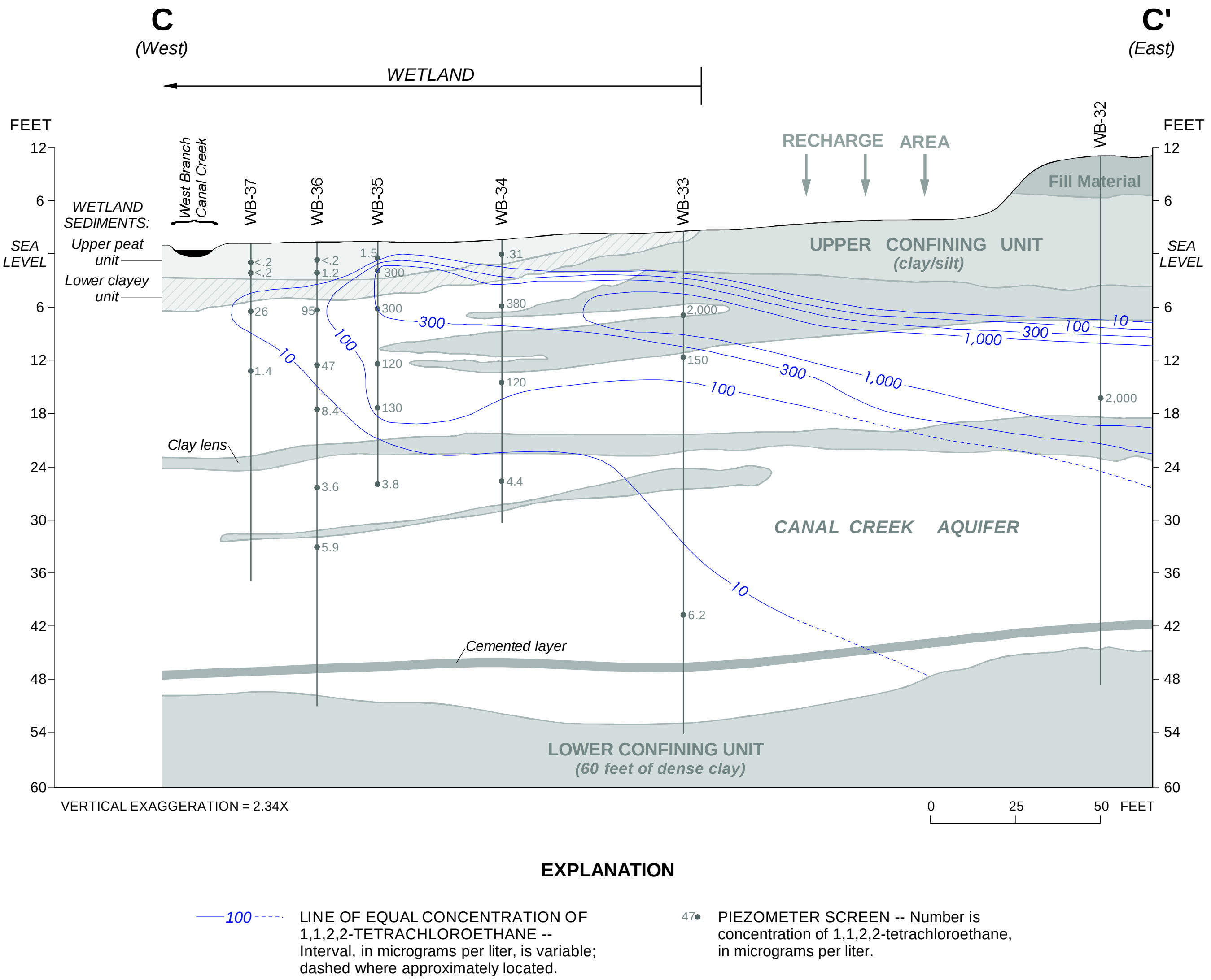
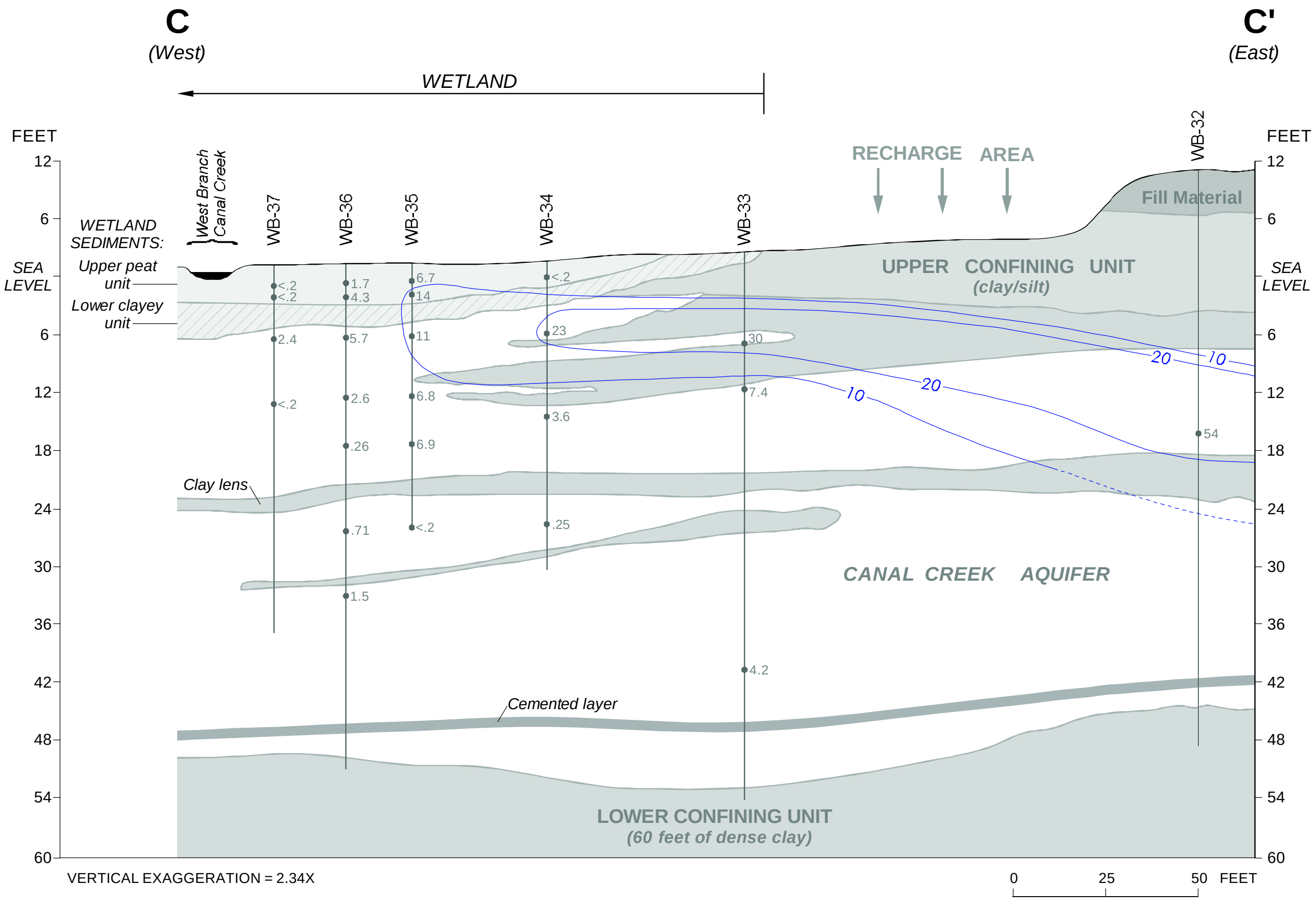


Figure 22. Section C-C' showing the distribution of 1,1,2,2-tetrachloroethane (PCA) in ground water, June-October 1995.



EXPLANATION

—10 - - -	LINE OF EQUAL CONCENTRATION OF TRICHLOROETHYLENE -- Interval, in micrograms per liter, is variable; dashed where approximately located.
11●	PIEZOMETER SCREEN -- Number is concentration of trichloroethylene, in micrograms per liter.

Figure 23. Section C-C' showing the distribution of trichloroethylene (TCE) in ground water, June-October 1995.

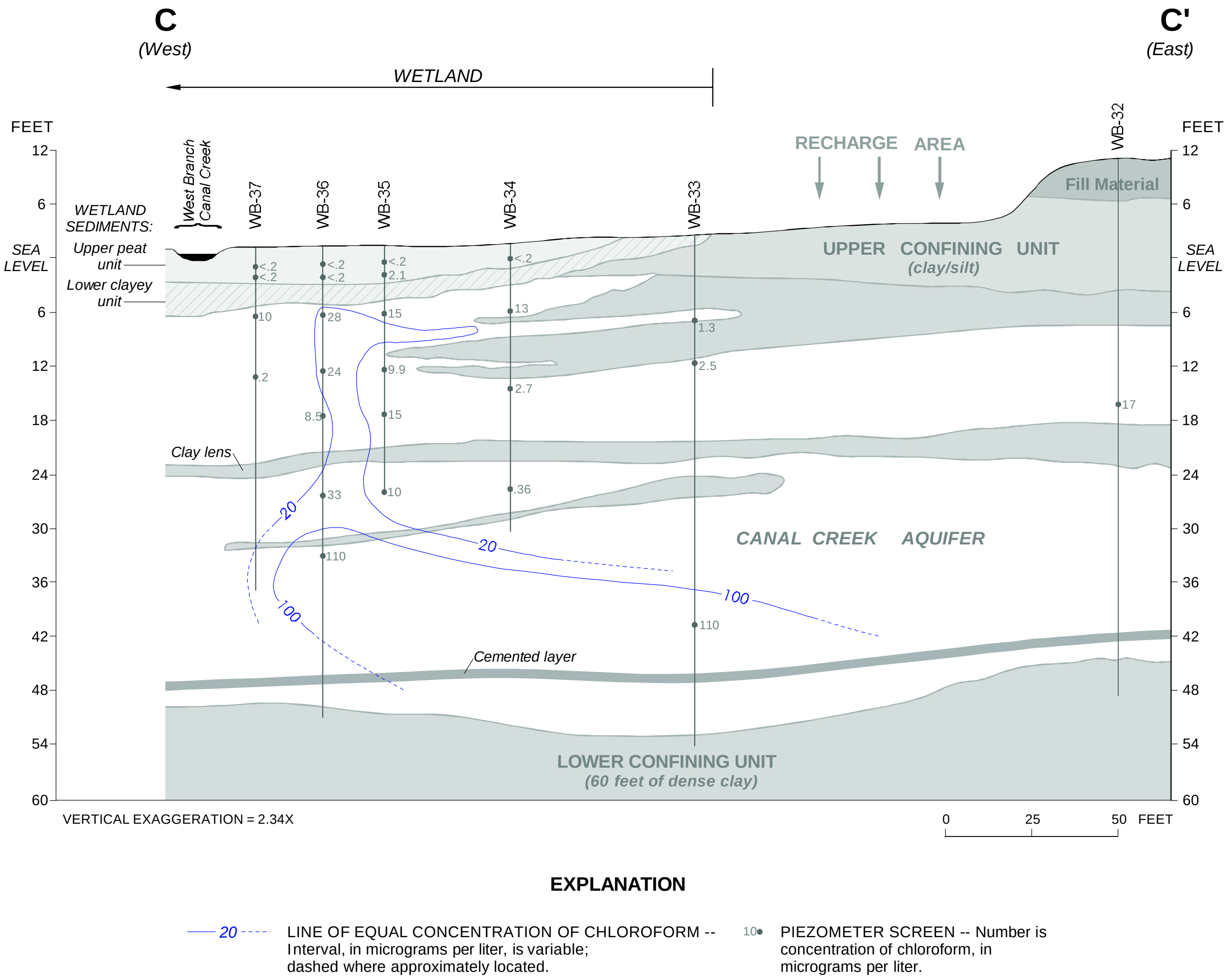


Figure 24. Section C-C' showing the distribution of chloroform (CF) in ground water, June-October 1995.

Table 4. *Median concentrations of major volatile organic compounds in ground-water samples collected during four sampling periods from piezometers screened in the wetland sediment and aquifer in the West Branch study area, Aberdeen Proving Ground, Maryland*

[TCE, trichloroethylene; PCA, 1,1,2,2-tetrachloroethane; CF, chloroform; CT, carbon tetrachloride; <, less than. All concentrations are in micrograms per liter]

Sample date	TCE	PCA	CF	CT	Number of samples
Wetland Sediment:					
June-October 1995	1.8	0.18	<0.2	<0.2	16
March-April 1996	1.8	<.2	<.2	<.2	17
June 1996	1.5	1.3	<.2	<.2	17
August 1996	2.2	1.0	<.2	<.2	17
Aquifer					
June-October 1995	58	94	55	27	11
March-April 1996	64	110	81	36	9
June 1996	66	89	82	33	11
August 1996	130	96	97	56	11

standard deviation (RSD) observed for duplicate samples analyzed for VOC's usually was less than 30 percent, averaging between 15 and 20 percent for samples analyzed at the two laboratories (Olsen and others, 1997). Median concentrations of TCE and PCA in water from the wetland sediment varied from 1.5 to 2.2 µg/L and from less than 0.2 to 1.3 µg/L, respectively. This variability could be due largely to analytical variability because the RSD's for duplicate samples were sometimes higher than 30 percent for water with concentrations less than 5 µg/L (Olsen and others, 1997).

The seasonal range in the median concentrations for CF and CT in the aquifer was greater than would be expected from sampling and analytical precision. Median concentrations of CF and CT in the aquifer were about 60 percent lower during the June-October 1995 sampling period (55 and 27 µg/L, respectively) compared to August 1996 (97 and 56 µg/L, respectively). The median concentrations of CF and CT in the aquifer were approximately the same during the March-April 1996 and June 1996 sampling periods (table 4).

The high range in median concentrations of the parent contaminants in the aquifer resulted primarily from an increase in concentrations at a couple of sites along section A-A' in August 1996 (fig. 25). Concentrations of TCE, PCA, CF, and CT in water from piezometers WB-24E and WB-26F, which are screened in the aquifer between 15 and 17 ft below land surface, were approximately twice as high in August 1996 compared to the other sampling periods. In addition, the four VOC's were not detected in WB-24B, which is screened above WB-24E in the upper peat unit at a depth of 3.0 to 3.5 ft below land surface, until a substantial increase in concentrations was observed during August 1996.

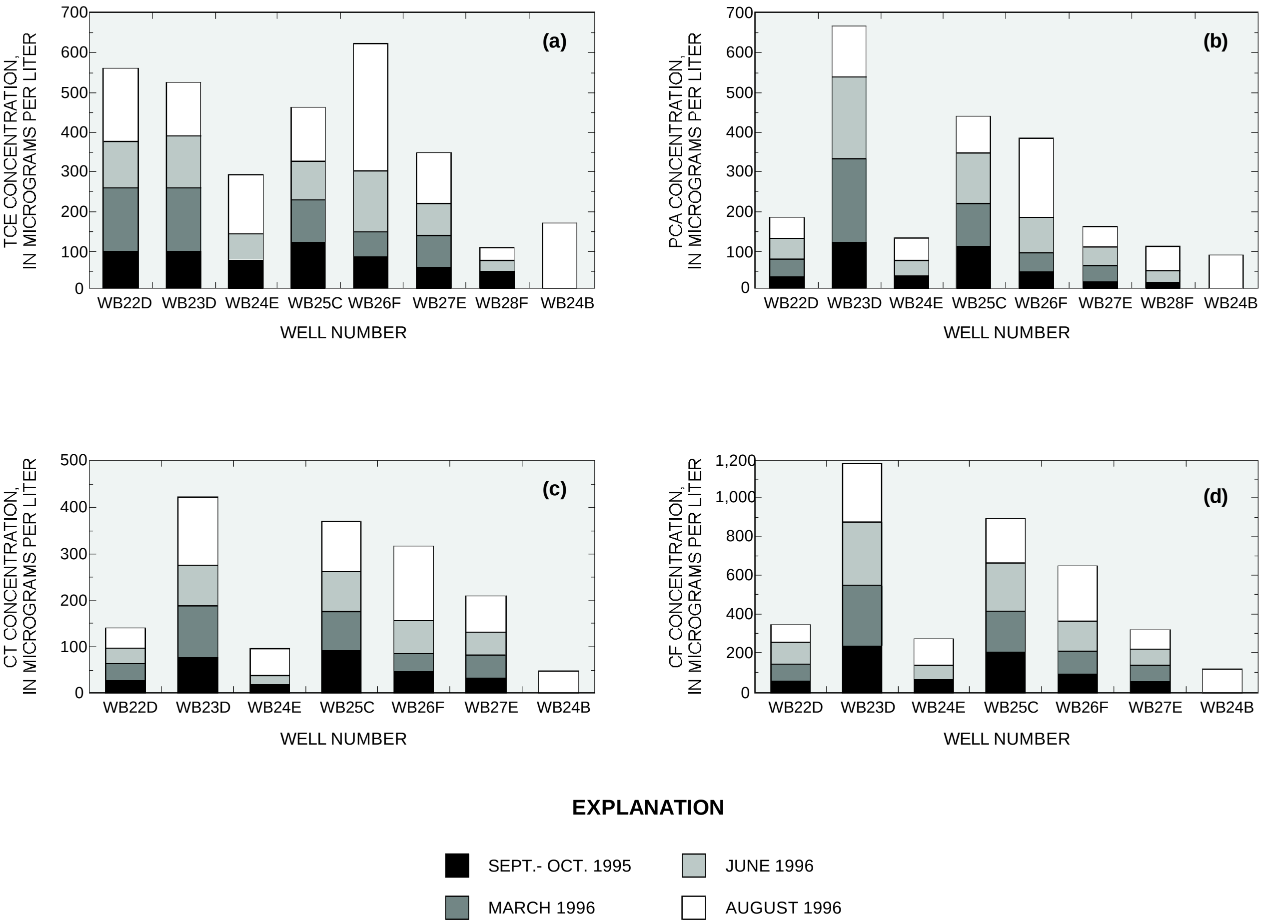


Figure 25. Seasonal changes in concentrations of **(a)** trichloroethylene (TCE); **(b)** 1,1,2,2-tetrachloroethane (PCA); **(c)** carbon tetrachloride (CT); and **(d)** chloroform (CF) in selected piezometers along section A-A'.

Concentrations of TCE, PCA, CF, and CT in WB-24B increased to 160, 81, 43, and 110 µg/L, respectively, in August 1996.

The increased concentrations observed in samples from these piezometers in August 1996 raises the question of whether natural attenuation processes in the wetland sediments could remediate the higher influx of contaminants. The increased flux of VOC's into the peat unit at site WB-24 seemed to be largely attenuated before land surface was reached because concentrations remained low in the piezometer screened about 1.5 ft above WB-24B (WB-24A). Concentrations of TCE, PCA, CF, and CT were less than detection in samples from WB-24A until the August 1996 sampling period (Olsen and others, 1997). In August 1996, PCA and chloroform concentrations in WB-24A increased to 3.4 µg/L (1.0 µg/L in a duplicate sample) and 1.5 µg/L (less than 0.2 µg/L in a duplicate sample), respectively, while TCE and CT concentrations remained below detection. At site WB-26, no increase in concentrations of the parent VOC's was observed in August 1996 in water from the wetland sediment, although three piezometers that are screened above WB-26F were sampled. Because samples were not collected after August 1996, it is not possible to determine whether higher concentrations of VOC's were transported to shallower depths in the wetland sediments after this date.

The increased concentrations of the parent VOC's measured during August 1996 at these sites were most likely associated with changes in hydrologic conditions, rather than changes in natural attenuation processes such as biodegradation or volatilization. Volatilization and biodegradation rates would be expected to increase during warmer seasons and cause a decrease, rather than an increase, in concentrations of the parent VOC's compared to cooler seasons. Head distributions did indicate a greater amount of contaminated ground water flowing westward into section A-A' during 1996 than 1995 because of an increase in recharge from precipitation during 1996 (figs. 10 and 14). The shallow ground water in the wetland area causes flow conditions to be more transient than might be expected in many deeper ground-water systems. Long-term monitoring would assist in evaluating the effects of transient flow conditions on contaminant transport and attenuation.

Distribution of Redox-Sensitive Constituents and Other Geochemical Parameters

Because the possible pathways and rates of biodegradation of the chlorinated VOC's are largely dependent on redox conditions, the redox state of the ground water needs to be determined to evaluate natural attenuation. The redox state of the ground water is determined from the distributions of dissolved oxygen, ferrous [Fe(II)] and ferric [Fe(III)] iron, sulfate and sulfide, and methane that were measured during the June-October 1995 sampling period. The redox zones that were delineated during this period generally did not change throughout the four other sampling periods in 1995-96, although only a limited number of piezometers were sampled during each of these periods. The concentrations of manganese and nitrogen species also were determined in the ground water, but these concentrations were low compared to those of other possible electron acceptors and by-products of microbial metabolism (Olsen and others, 1997).

Other geochemical parameters that can affect natural attenuation processes include DOC, alkalinity (as bicarbonate), and pH. Concentrations of DOC indicate the availability of substrates to provide electron donors during reductive dechlorination of VOC's. Alkalinity concentrations tend to increase during microbial respiration when oxidation of DOC is coupled to reduction of dissolved oxygen, nitrate, iron, and sulfate. Increases in alkalinity above background levels inside a contaminant plume can indicate that microbial degradation of contaminants or natural DOC is occurring through oxidation reactions. The pH can affect the presence and activity of microbial populations. Microbes capable of degrading chlorinated VOC's generally prefer pH values between 6 to 8 standard units, although they can be active in a wide range of conditions.

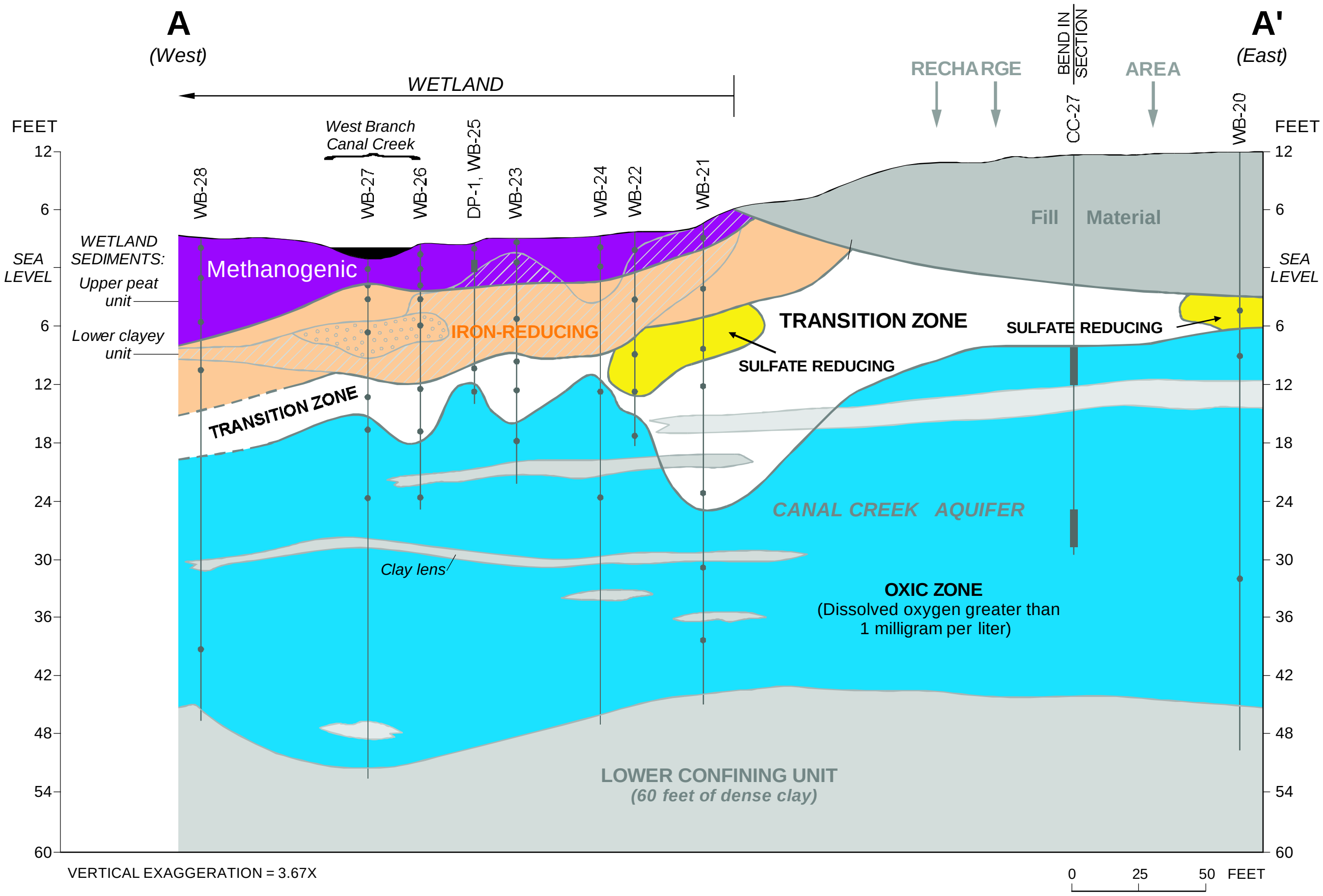
Section A-A'

The distribution of redox-sensitive constituents in ground water along section A-A' shows that the aquifer generally was either aerobic or hypoxic, whereas anaerobic conditions existed in the wetland sediments (fig. 26). In the aquifer, dissolved-oxygen concentrations were greater than 1 mg/L, except for a thin transition zone where concentrations were less than or equal to 1.0 mg/L. The transition zone in the aquifer extended from the most contaminated well upgradient of the wetland (CC-27A) and is located immediately beneath the wetland sediments. Although dissolved-oxygen concentrations in this transition zone indicate either hypoxic or anaerobic conditions, concentrations of Fe(II), sulfide, and methane were low or below detection. Thus, the more strongly reducing conditions that are needed for rapid and complete reductive dechlorination of the major VOC's were not present in the aquifer. Aerobic oxidation of the major VOC's also would not be likely. Methane or other compounds such as toluene that are required as primary substrates by the micro-organisms capable of oxidizing the chlorinated VOC's were not present in the aquifer. The distribution of redox-sensitive constituents in the aquifer, therefore, is consistent with the conceptual model that biodegradation of the chlorinated VOC's is not a significant attenuation process in the aquifer.

Some microbial degradation of natural or anthropogenic carbon compounds, however, is indicated by the decreased dissolved-oxygen concentrations in the transition zone and in comparison to background concentrations in the aquifer. Dissolved-oxygen concentrations within the contaminated region of the aquifer (figs. 16 and 26) typically were lower than background concentrations. Dissolved-oxygen concentrations ranged from 3.20 to 6.53 mg/L in the aquifer at the background site WB-19, whereas dissolved-oxygen concentrations were typically less than 2 mg/L in the contaminated aquifer along A-A' (fig. 27). The comparison to background concentrations indicates that consumption of the oxygen is at least partly caused by microbial oxidation of organic compounds associated with the plume. It is not clear, however, what these organic substrates in the aquifer are. Concentration of aromatic compounds such as benzene and toluene, which can be easily oxidized by microorganisms, were less than 5 µg/L at all sites in the aquifer along A-A' (Olsen and others, 1997). Measured concentrations of DOC, which did not include VOC's, also were low in the aquifer, ranging from 0.1 to 3.1 mg/L along section A-A'. In the transition zone, however, it is likely that downward flux at some locations during high tide transports DOC from the wetland sediments to the aquifer, resulting in an increased source of oxidizable substrates.

As hypothesized in the conceptual model, reducing conditions that are favorable for reductive dechlorination of the chlorinated VOC's are present in the wetland sediments. Conditions became increasingly reducing in the wetland sediments along the upward direction of ground-water flow from the aquifer (fig. 26). Iron-reducing conditions, characterized by Fe(II) concentrations greater than 1,000µg/L, were predominant in the lower clayey unit. Methanogenic conditions were predominant in the upper peat unit. Methane concentrations greater than 500 µg/L were used to define the methanogenic/mixed zone in figure 26, but concentrations commonly were on the order of several 1,000’sµg/L. During the comprehensive sampling (June-October 1995), the maximum methane concentration along section A-A' was 11,000 µg/L (fig. 26). In addition to high methane concentrations, relatively high concentrations of Fe(II) and sulfide were common in this zone. Concentrations of Fe(II) and sulfide in this methanogenic/mixed zone were as high as 26,100 µg/L and 190 µg/L, respectively.

These reducing conditions seem to exist naturally in the wetland sediments because similar conditions were observed at the background site and contaminated sites. For example, figure 27 shows the concentrations of redox-sensitive constituents and other geochemical parameters measured with depth at site WB-26, which showed concentration profiles typical along section A-A', and at the background site WB-19. Dissolved oxygen decreased in the aquifer along the upward direction of flow at both sites. As the wetland sediments (and the paleochannel deposit at WB-26) are reached, reducing conditions became evident by the increase in Fe(II), sulfide,



EXPLANATION

● PIEZOMETER SCREEN

☐ TRANSITION ZONE -- Concentrations of dissolved oxygen less than 1.0 milligrams per liter; concentrations of iron, sulfide, and methane less than those observed in anaerobic zones.

ANAEROBIC ZONES:

🟧 IRON-REDUCING ZONE -- Concentrations of ferrous iron greater than 1,000 micrograms per liter.

🟨 SULFATE-REDUCING ZONE -- Concentrations of sulfide greater than 100 micrograms per liter.

🟪 METHANOGENIC / MIXED ZONE -- Concentrations of methane greater than 500 micrograms per liter; concentrations of ferrous iron and sulfide greater than 1,000 and 100 micrograms per liter, respectively, at some locations.

Figure 26. Section A-A' showing the predominant redox zones in ground water, June-October 1995.

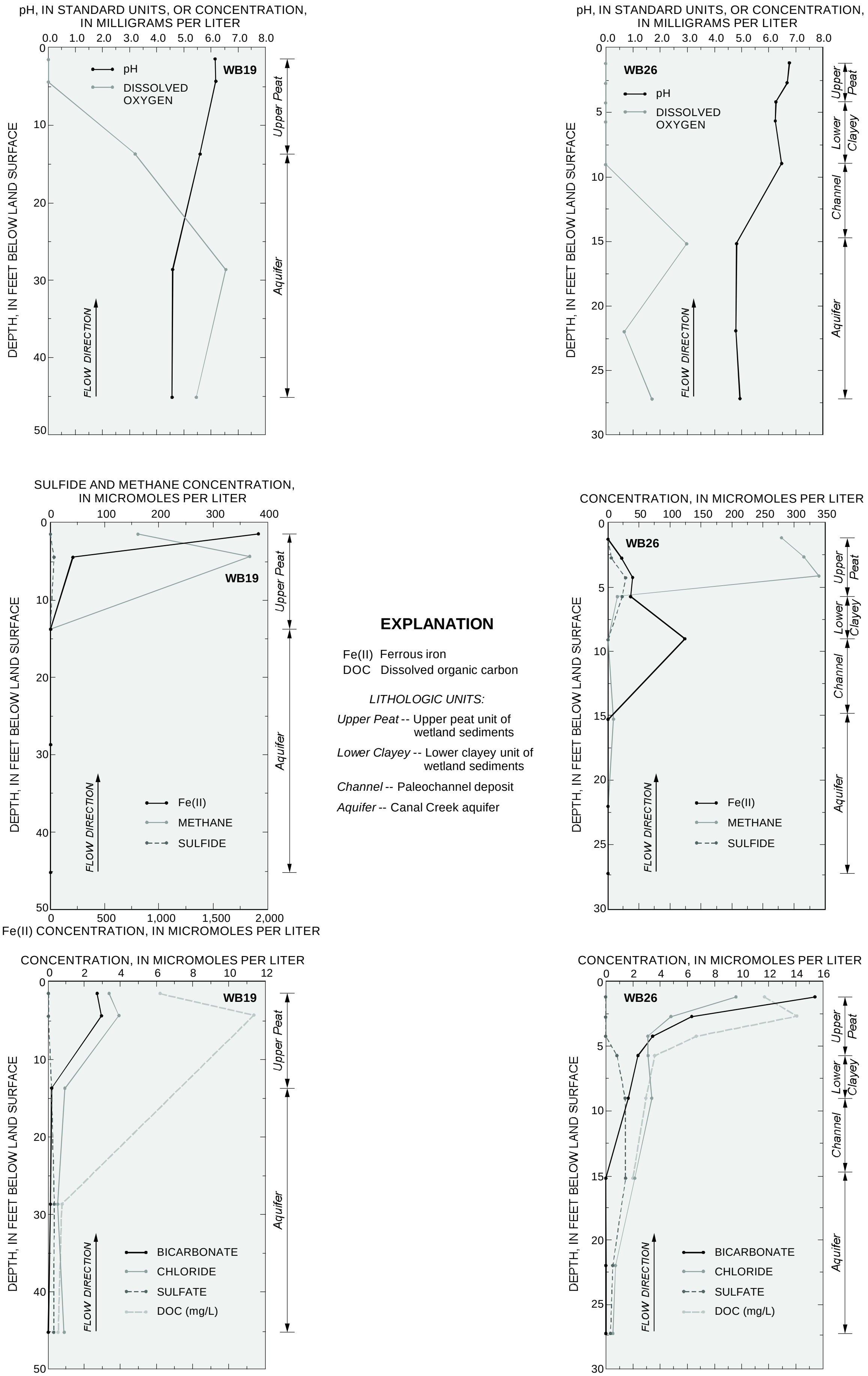


Figure 27. Changes in concentrations of selected redox-sensitive constituents and geochemical parameters with depth at site WB-26 and at the background site WB-19, June-October 1995.

and methane concentrations. Iron reduction, rather than sulfate-reduction, seemed to be the predominant terminal electron-acceptor process for microbial respiration in the lower part of the wetland sediments at both sites. Sulfate concentrations in the ground water were relatively low in this freshwater environment, whereas abundant iron minerals are present in the aquifer and wetland sediments. Sulfate concentrations, however, were elevated in the aquifer at site WB-26 and other sites along section A-A' compared to background levels. Sulfate concentrations in the aquifer at WB-26 were as high as 1.5 mmol/L, whereas the maximum concentration at site WB-19 was 0.32 mmol/L in June-October 1995 (fig. 27). The elevated sulfate concentrations at WB-26 resulted in greater sulfide production compared to background. In addition, Fe(II) and sulfide concentrations decreased throughout the upper peat at site WB-26, and methanogenesis became the predominant process. Although methane concentrations were high in the peat at the background site, concentrations of Fe(II) continued to increase (fig. 27).

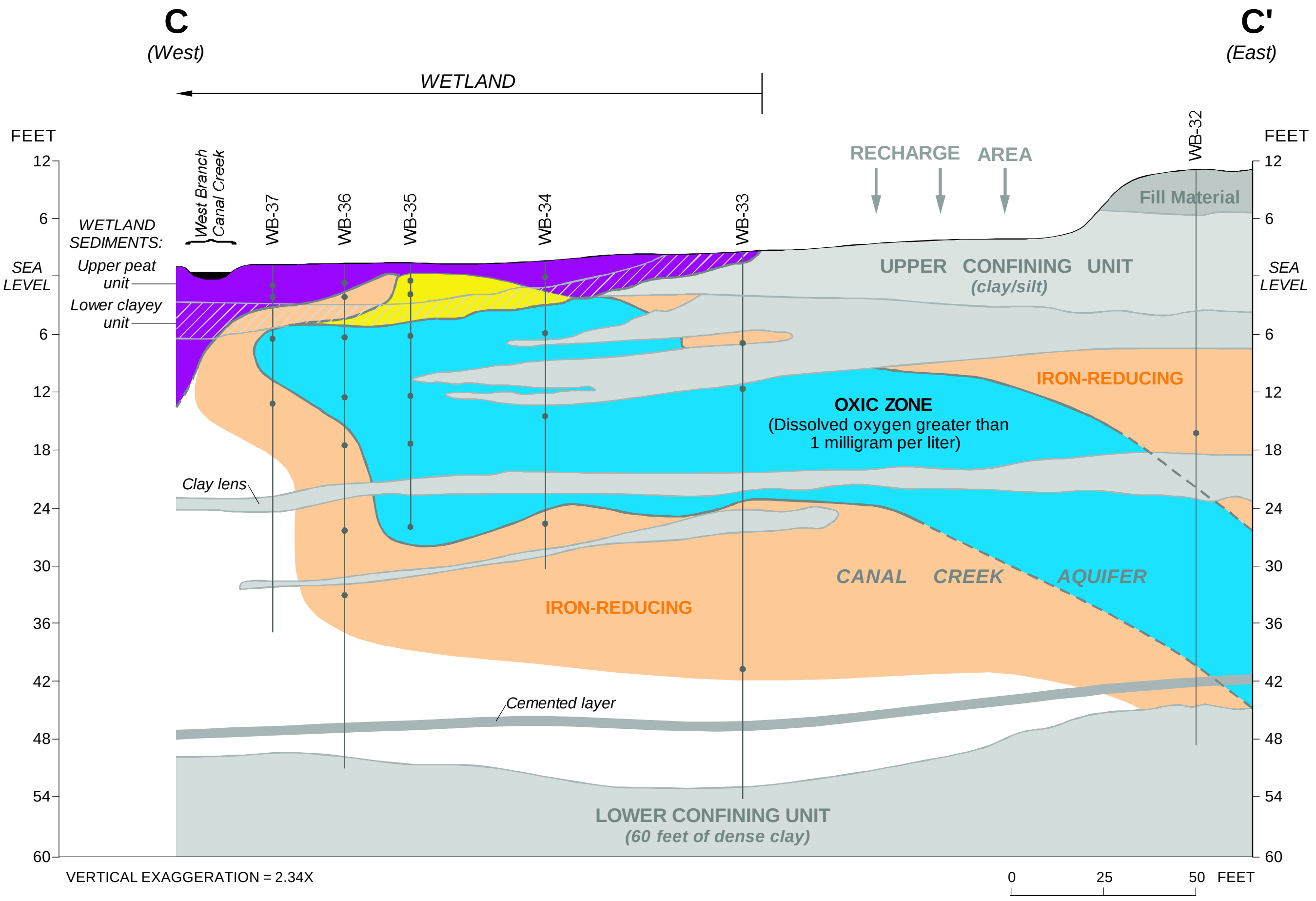
These differences are probably caused by precipitation of iron sulfide minerals in the wetland sediment at WB-26, where sufficient sulfide production is occurring. Pyrite was detected in mineralogical analyses of the wetland sediments at and near site WB-26. The elevated sulfate concentrations compared to background at site WB-26 could be associated with the contaminant plume and/or with surface-water intrusion. Brines, which may have contained elevated sulfate along with high sodium and chloride, were stored upgradient of the wetland on the western side of the creek during operation of a chloride plant (Lorah and Clark, 1996, p. 77). Sulfate concentrations in the surface water (Olsen and others, 1997) had a median of 1.1 mmol/L, which is similar to the maximum concentration detected in the aquifer at site WB-26. Because site WB-26 is adjacent to the creek channel where reversals in head gradients were observed at high tide, surface-water intrusion would be greater than at the background site.

Concentrations of DOC increased in the wetland sediments compared to the aquifer, indicating that natural carbon substrates are available to support increased microbial activity in the wetland sediments (fig. 27). Concentrations of DOC in the upper peat unit were as high as 16 and 11 mg/L, respectively, along section A-A' and at the background site. Other indications of the naturally high microbial activity in the wetland sediments are the increase in pH and bicarbonate as ground water flows upward from the aquifer, both within the contaminant plume and at the background site (fig. 27). Microbial activity generates carbon dioxide (or dissolved bicarbonate), and consumption of hydrogen ions (H^+) during iron and sulfate reduction can cause the pH of the water to increase. Alteration of the feldspars present in the wetland sediments, however, could also increase the pH of the ground water (Drever, 1988, p.157). The aquifer was naturally acidic, as indicated by pH values of 4.54 to 5.60 in the aquifer at site WB-19. The pH in the wetland sediments generally ranged between 6 and 7, which is in the optimum range for most microbial populations associated with reductive dechlorination of the VOC's.

Section C-C'

In section C-C', the same general pattern as section A-A' was seen of increasingly reducing conditions along the upward direction of flow through the wetland sediments. Some differences, however, were observed in the redox zones in ground water along section C-C' compared to A-A' (figs. 26 and 28). The aquifer underlying the wetland sediments along C-C' did not have the transition zone observed along A-A' and instead had dissolved-oxygen concentrations ranging from 1.11 to 3.18 mg/L. Around the edges of this oxic zone in the aquifer, relatively high Fe(II) concentrations indicated that iron-reduction was a predominant electron-acceptor process. The iron-reducing areas observed in the aquifer did not always coincide with the most contaminated areas (figs. 20 and 28).

In addition, the redox state of the ground water was not always lowered below iron-reducing conditions by the time it flowed through the lower clayey unit and into the upper peat unit, as was generally observed along A-A'. Iron-reduction seemed to be the predominant process in water



EXPLANATION

● PIEZOMETER SCREEN

ANAEROBIC ZONES:

🟧 IRON-REDUCING ZONE -- Concentrations of ferrous iron greater than 1,000 micrograms per liter.

🟨 SULFATE AND IRON-REDUCING ZONE -- Concentrations of sulfide greater than 100 micrograms per liter, and concentrations of ferrous iron greater than 1,000 micrograms per liter.

🟪 METHANOGENIC / MIXED ZONE -- Concentrations of methane greater than 500 micrograms per liter; concentrations of ferrous iron and sulfide greater than 1,000 and 100 micrograms per liter, respectively, at some locations.

Figure 28. Section C-C' showing the predominant redox zones in ground water, June-October 1995.

collected from the upper peat unit at one piezometer at site WB-36, and water collected from the two piezometers at WB-35 that are screened in the upper peat unit showed a mixed sulfate- and iron-reducing zone. Methanogenesis was the predominant electron-acceptor process in the upper peat unit at other locations along section C-C'. Methane concentrations at these sites, however, were somewhat lower than observed along section A-A'.

The iron and sulfate-reducing zones in the upper peat unit correspond to the area where the greatest upward discharge from the aquifer was indicated from head distributions, especially at high tide (figs. 11 and 12). Thus, the less reducing conditions probably result from a relatively higher amount of dissolved-oxygen flux into the wetland sediments compared to other areas along section C-C'. In addition, although the estimated linear flow velocities were similar along vertical flowpaths in sections A-A' and C-C', the lower wetland sediment unit is thinner along section C-C' and, thus, provides less area for reactions that consume dissolved oxygen and other electron acceptors to occur before the upper peat is reached. The thinness of the lower clayey unit of the wetland sediments along section C-C' also seems to affect the pH of the ground water (fig. 29). Along section A-A', the naturally acidic water in the aquifer generally increased to between 6 and 7 by the time the water flowed through the lower clayey unit (for example, site WB-26 in fig. 27). Along section C-C ', however, pH ranged from 4.41 to 5.23 in the zone where greatest ground-water discharge from the aquifer occurred (figs. 11, 12, and 29). The lower pH may initially inhibit methanogenesis (DeLaune and others, 1986; Beeman and Suflita, 1990).

Results from peepers installed at sites WB-35, WB-36, and WB-37, however, showed that methane production was substantial within 0 to 2 ft below land surface in the upper peat unit. For example, methane concentrations that were measured in peepers at sites WB-35 and WB-36 were as high as 10,000 and 14,000 µg/L, respectively, in June 1996 (fig. 21). The extreme changes that occurred over very small vertical scales in the wetland sediment are evident in the methane increase from about 4,000 to 10,000 µg/L over a 3-in. interval at site WB-35 (between 9 and 12 in. below land surface on fig. 21a). Similar methane concentrations were measured in peepers installed in November-December 1995 and March 1996. Higher sulfide concentrations also were observed at site WB-35 in peeper samples than those measured in water from the piezometers screened in the wetland sediment. Sulfide concentrations in a peeper installed in June 1996 were greater than 2,000 µg/L at depths between 11 and 24 in. below land surface, whereas the sulfide concentrations were 1,300 and 90 µg/L, respectively, in WB-35A and WB-35B on this date.

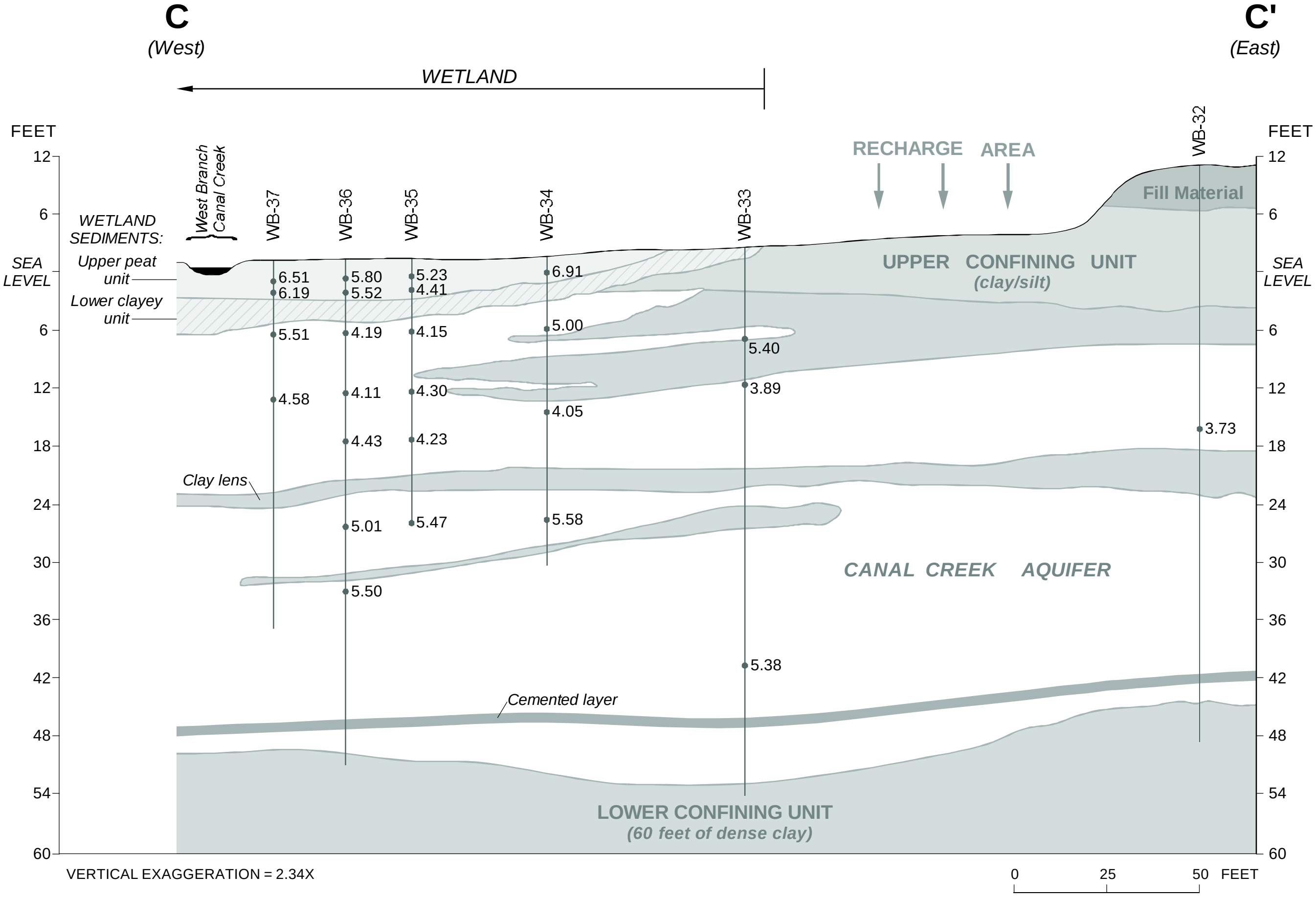
Biodegradation and Abiotic Degradation

Anaerobic Processes

Although the reduction in concentrations of the parent VOC's and the presence of anaerobic conditions in the wetland sediments along West Branch Canal Creek suggest that anaerobic biodegradation could occur, further information is needed to determine if biodegradation is actually a major natural attenuation process. The distribution of possible daughter products of TCE and PCA in the ground water are discussed below, providing further field evidence that anaerobic biodegradation is occurring. Laboratory microcosm experiments conducted under anaerobic conditions with TCE and PCA confirmed field evidence of the major degradation pathways and allowed potential degradation rates to be calculated.

Field Evidence

Along both section A-A' and C-C', the relative proportions of parent VOC's to possible anaerobic degradation products differed substantially in water in the aquifer compared to water in the wetland sediment (fig. 30). Relatively high concentrations of the parent compounds TCE and PCA were measured in the aquifer, whereas concentrations of daughter products were low or undetectable. Little reductive dechlorination of TCE and PCA, therefore, seemed to occur in the aquifer, even downgradient where the dissolved-oxygen concentrations were less than 1 mg/L beneath the wetland sediments along section A-A' (fig. 26). In contrast, concentrations of the



EXPLANATION

4.05● PIEZOMETER SCREEN -- Number is pH value, in standard units.

Figure 29. Section C-C' showing the pH measured in ground water, June-October 1995.

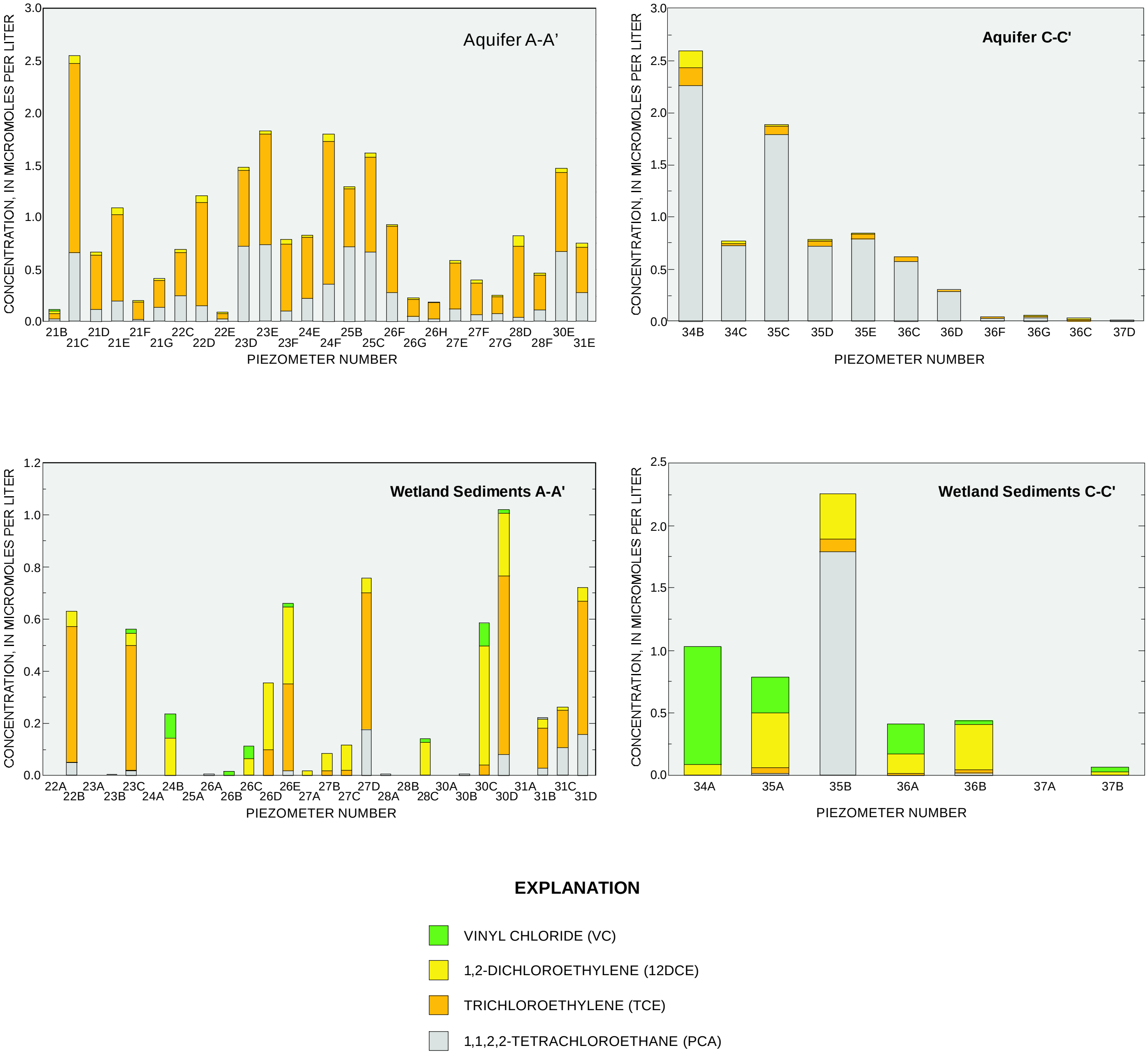


Figure 30. Concentrations of the parent contaminants trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA) and of the anaerobic daughter products 1,2-dichloroethylene (12DCE) and vinyl chloride (VC) in water in the aquifer compared to water in the wetland sediments along sections A-A' and C-C', June-October 1995. [*Note variation in scale.*]

parent compounds were low, or in many cases, undetectable in the more reducing environment of the wetland sediments, and the daughter products 12DCE and VC were present in relatively high concentrations (figs. 26, 27, and 30). These daughter products could be produced from TCE biodegradation by hydrogenolysis and from PCA degradation through hydrogenolysis and dichloroelimination pathways (fig. 5). The daughter products 112TCA and 12DCA, which can be produced by hydrogenolysis of PCA (fig. 5), also were commonly observed in the anaerobic wetland sediments but generally not in concentrations as high as observed for 12DCE and VC.

Although concentrations of these anaerobic degradation products in water in the wetland sediments were high relative to concentrations in the aquifer, total concentrations of the VOC's decreased upward, as discussed earlier. Figure 31 clearly shows the vertical change in the relative concentrations of parent and daughter compounds with depth in the aquifer and wetland sediments, using results from site WB-26 along section A-A'. Similar vertical profiles were observed at all contaminated sites in the wetland. Again, only concentrations of the parent compounds TCE and PCA were relatively high in the aquifer. Moving upward in the direction of ground-water flow, the concentrations of TCE and PCA decreased markedly in the paleochannel deposit and the lower clayey unit of the wetland sediments where iron-reducing conditions existed (fig. 27 and 31). Sorption could account for some removal of the TCE and PCA from water in the wetland sediment, but the presence of these known daughter products indicates that biodegradation also is occurring. Although 12DCE is the predominant daughter product that was initially present above the aquifer, lower concentrations of VC, 112TCA, and 12DCA were also produced.

In the upper peat unit, the parent compounds were no longer detectable, and 12DCE and VC were the predominant daughter products detected. The VC concentrations increased between the lower clayey unit and the upper peat unit of the wetland sediments, concomitant with the rise in methane concentrations in this unit (figs. 27 and 31). This relation between VC and methane concentrations agrees with other studies that have shown that reductive dechlorination of 12DCE to VC requires the extremely reducing conditions of methanogenesis (for example, Bagley and Gossett, 1990). Few data are available in the literature on the reducing conditions required for dichloroelimination of 112TCA, which also can produce VC. It is interesting to note, however, that low concentrations of 112TCA and VC appeared together in the paleochannel deposit where iron-reducing conditions characterized the redox state of the water. Because 112TCA was not observed above this sampling point, the VC that was observed in the upper peat unit probably resulted from hydrogenolysis of 12DCE.

The decrease in 12DCE and VC concentrations to below detection levels near land surface could result from further hydrogenolysis to the non-chlorinated and nontoxic end products of ethene and ethane. Ethene and ethane were rarely detected in the ground-water samples, but these compounds could be converted to carbon dioxide and cell material by microorganisms as quickly as they are produced. Aerobic oxidation, either through direct or cometabolic microbial reactions, and volatilization are other possible attenuation mechanisms for the 12DCE and VC. Aerobic oxidation could occur close to the air-water interface or near plant roots where oxygen could be available. In addition, recent microcosm experiments have shown that vinyl chloride can be oxidized under iron-reducing conditions, especially if organic ligands are present to increase the bioavailability of Fe(III) (Bradley and Chapelle, 1996).

Because both TCE and PCA were significant parent contaminants along section A-A', their relative importance in producing the 12DCE and VC cannot be assessed there. The primary parent compound discharging from the aquifer along section C-C', however, was PCA, and 12DCE and VC were also the dominant daughter products detected here in the wetland sediment. Figure 32 shows the vertical distributions of parent and daughter compounds measured in a 2-ft interval from a peeper installed at site WB-35; concentrations are also shown for the piezometer WB-35B, which is screened near the base of the upper peat unit with the midpoint of the 6-in.

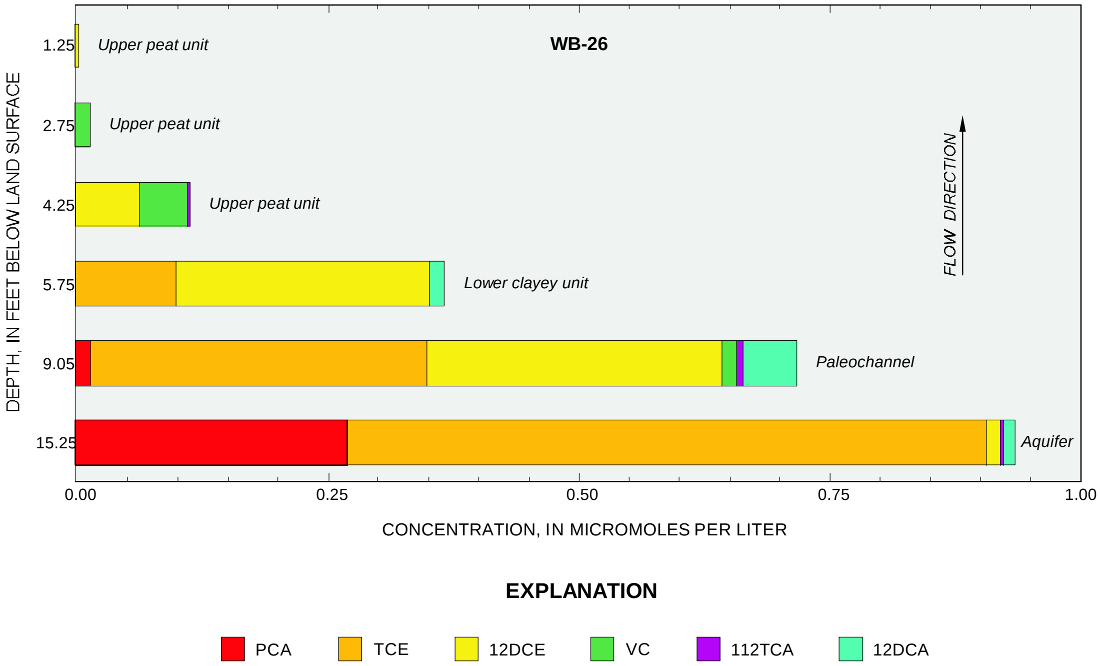


Figure 31. Vertical distribution of the parent contaminants trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA) and of the anaerobic daughter products 1,2-dichloroethylene (12DCE) and vinyl chloride (VC) at site WB-26, June-October 1995.

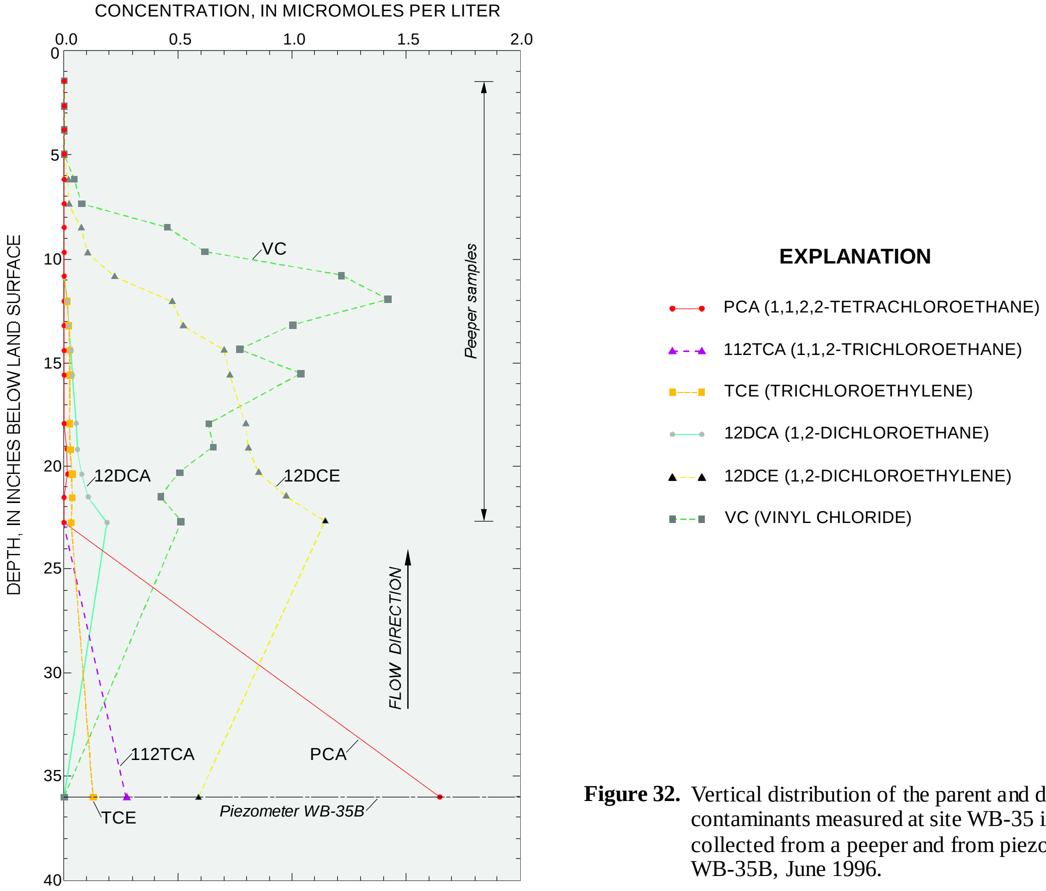


Figure 32. Vertical distribution of the parent and daughter contaminants measured at site WB-35 in water collected from a peeper and from piezometer WB-35B, June 1996.

screen at a depth of 36 in. Because the concentrations of TCE were less than 3 percent of the PCA concentrations in the aquifer along section C-C', all the 12DCE could not result from hydrogenolysis of TCE. These results indicate that dichloroelimination, which produces 12DCE, was the major degradation pathway for PCA. Some 112TCA was present in water collected from WB-35B but not from the peeper. Dichloroelimination of the 112TCA could have produced some of the VC observed in the deepest peeper sampling points. However, the continued increase in VC concentrations as 12DCE concentrations decreased along the flowpath indicates that hydrogenolysis of the 12DCE (produced from dichloroelimination of the PCA) also was occurring (fig. 32). The maximum concentrations of VC coincided with the highest concentrations of methane (fig. 21a), as noted above for site WB-26. Concentrations of VC reached a maximum at a depth of about 11.5 in. below land surface, where methane concentrations began to rise sharply from about 5,000 to 10,000 µg/L during this sampling period (figs. 21a and 32). Total concentrations of the daughter products were as high as about 2.0 µmol/L (170 µg/L) during this sampling period but decreased below detection levels within 6 in. of land surface. The vertical distributions of the VOC's and redox constituents that were obtained from the peepers allow the possible degradation pathways to be defined in these thin wetland sediments in a detailed manner that would not have been possible with only the piezometer data.

Reductive dechlorination in the wetland sediments also could be a major mechanism of natural attenuation for the CT and CF that were present in the aquifer. CT can be degraded to CF and then to methylene chloride and carbon dioxide in a sequential hydrogenolysis reaction under anaerobic conditions (Bouwer, 1994). Because CT and CF were known to have been released together as wastes in the area, the significance of this degradation pathway cannot easily be evaluated on the basis of the field data. The fact that CT and CF were commonly not detected in the anaerobic wetland sediments (figs. 19 and 24), however, indicates that degradation is occurring. Concentrations of methylene chloride, which is a common laboratory contaminant, were not significantly higher than concentrations observed in laboratory blanks (Olsen and others, 1997). If methylene chloride is produced, it is most likely oxidized or volatilized.

Water temperature can greatly influence biodegradation rates because metabolic activity of microorganisms can roughly double for every 10°C increase in temperature between 5 and 25°C (Cano and Colome, 1986, p. 181). Less biodegradation of the chlorinated VOC's, therefore, might occur in the cooler seasons if water temperature decreased in the wetland sediments. Water temperatures in piezometers screened in the wetland sediments were typically between 17 and 25 °C during the sampling periods of June-October 1995, June 1996, and August 1996 (Olsen and others, 1997). Water temperatures were substantially lower, ranging from 5.8 and 13.5 °C, during November-December 1995 and March-April 1996. A decrease in biodegradation rates during the cooler seasons might be distinguished by a decrease in the ratio of daughter products to parent compounds. Such a trend was not observed, however, in samples collected from the piezometers. The median ratio of daughter to parent VOC's ranged from about 4 to 7 over the sampling periods, and the ratio was the same during the warm period of June-October 1995 and the cool period of March-April 1996. The lack of a trend in the ratios of daughter to parent compounds may be an artifact of the large number of samples in which the parent concentrations were below detection in the shallow wetland sediments, where seasonal temperature changes were greatest. The ratios were undefined for these samples.

Because site WB-35 had the highest concentrations of VOC's at such shallow depths in the wetland sediment (figs. 16 and 20), seasonal trends in the data may be most easily distinguished at this site. In peepers installed at site WB-35, the maximum concentrations of total chlorinated VOC's varied from about 0.5 to 2.0 µmol/L between October 1995, March 1996, and June 1996 (0 to 24 in. below land surface in fig. 33). The only VOC's detected in the peepers were the anaerobic daughter products, whereas PCA was

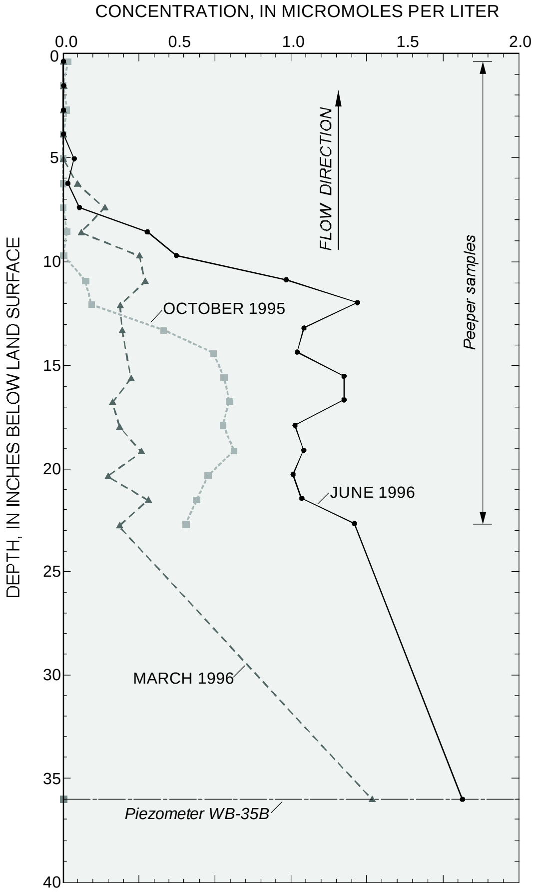


Figure 33. Vertical distribution of total concentrations of chlorinated volatile organic compounds in peepers installed at site WB-35 during October 1995, March 1996, and June 1996.

the primary VOC detected in the piezometer WB-35B (fig. 32). The peeper results showed a significant variation in the total amount of daughter products being produced, and this variation could be related to seasonal changes in temperature in the shallow sediments. The samples collected during the coolest periods, March 1996, had lower concentrations of daughter products than those during the warmer months of October 1995 and June 1996 (fig. 33). Although lower concentrations of daughter products were measured during March 1996 in the peeper, a higher breakthrough of the parent contaminant, PCA, was not observed in water in the shallow wetland sediments. The parent contaminant PCA had similar concentrations in the piezometer WB-35B during March 1996 and June 1996, but PCA was not observed in the peeper samples during either sampling period. Other attenuation processes, such as sorption, may be removing the PCA deeper in the wetland sediment and preventing its breakthrough to the shallow wetland sediments. It is also possible that the zone of greatest biodegradation during the cooler period of March 1996 occurred between the deepest peeper sampling point and the piezometer screen for WB-35B (24 to 36 in. below land surface) where temperatures might have been higher.

Laboratory Evidence

Rapid removal of TCE and PCA was observed in the microcosm experiments with wetland sediment and water under methanogenic conditions. Comparison of the decrease in concentrations in the non-sterile to the sterile controls indicates that biodegradation is a major removal mechanism (figs. 34 to 36), although abiotic removal processeswere initially significant. About 50 percent of the TCE and PCA that was added to the sterile and non-sterile microcosms at

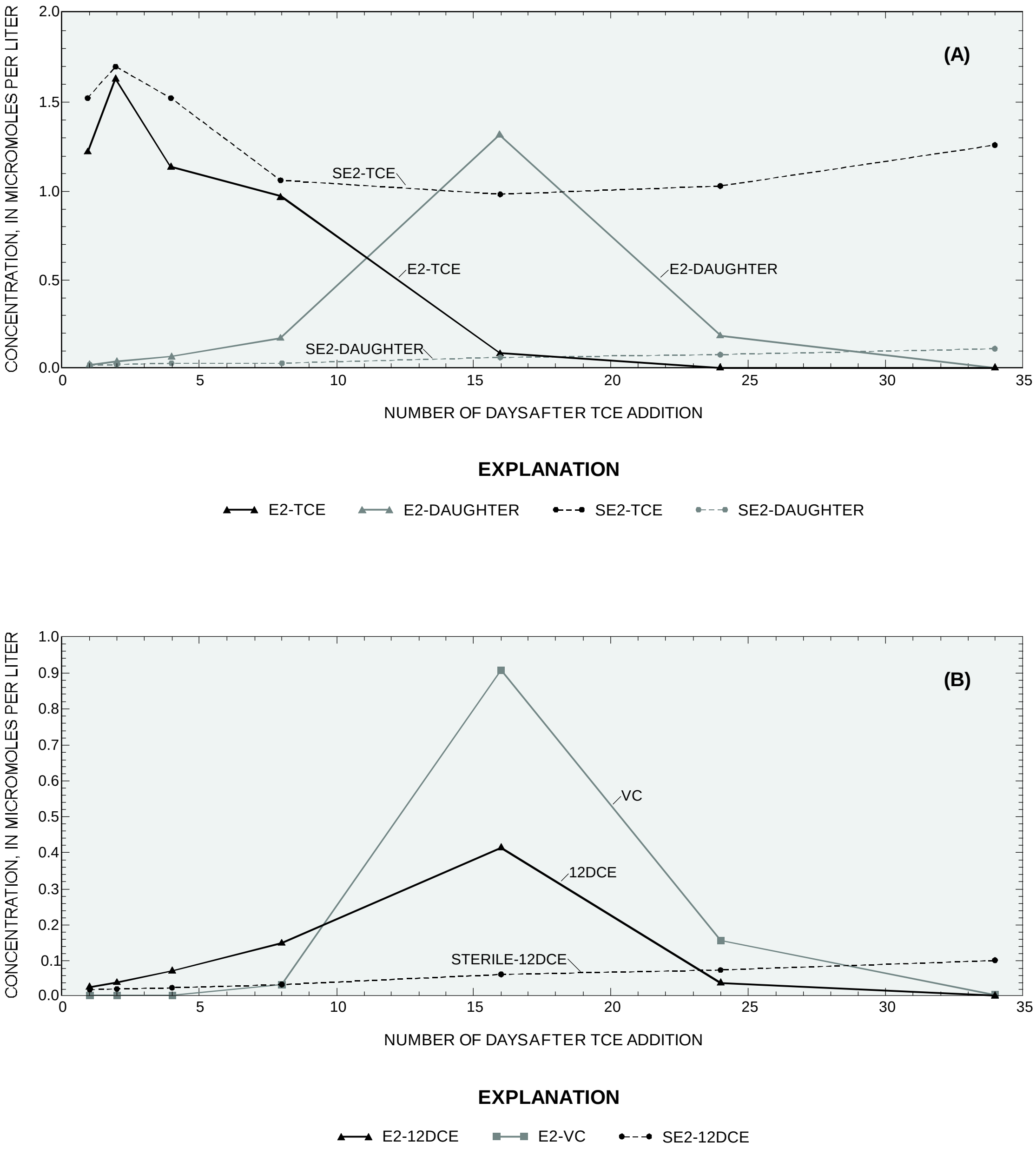


Figure 34. Degradation of trichloroethylene (TCE) under methanogenic conditions in microcosms amended with approximately 3.0 micromoles per liter of TCE at day 0. **(A)** Concentrations of TCE and the sum of daughter products in the non-sterile microcosms (E2) and sterile controls (SE2). **(B)** Concentrations of the daughter products, including the total of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene (12DCE) and vinyl chloride (VC).

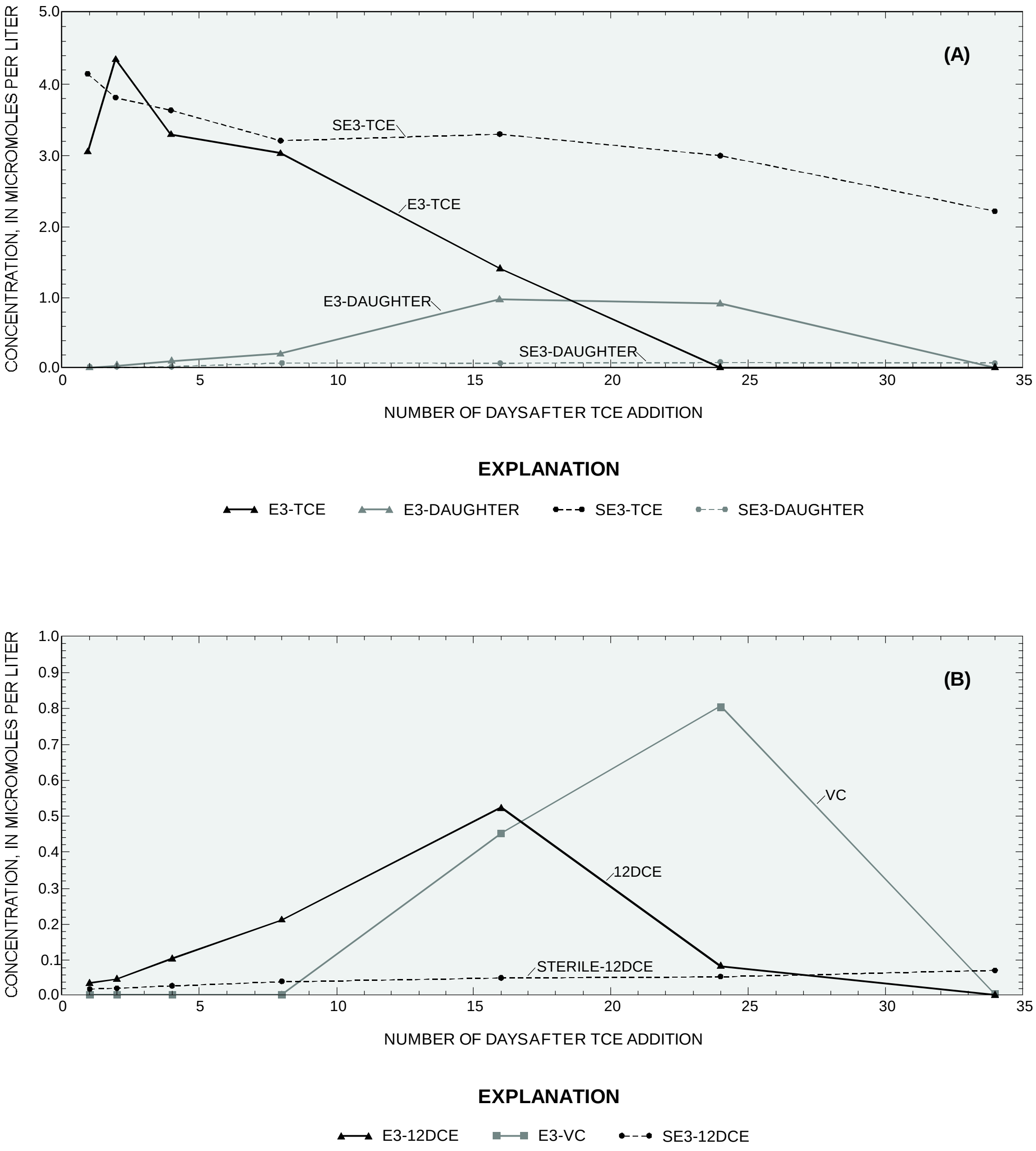


Figure 35. Degradation of trichloroethylene (TCE) under methanogenic conditions in microcosms amended with approximately 7.5 micromoles per liter of TCE at day 0. **(A)** Concentrations of TCE and the sum of daughter products in the non-sterile microcosms (E3) and sterile controls (SE3). **(B)** Concentrations of the daughter products, including the total of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene (12DCE) and vinyl chloride (VC).

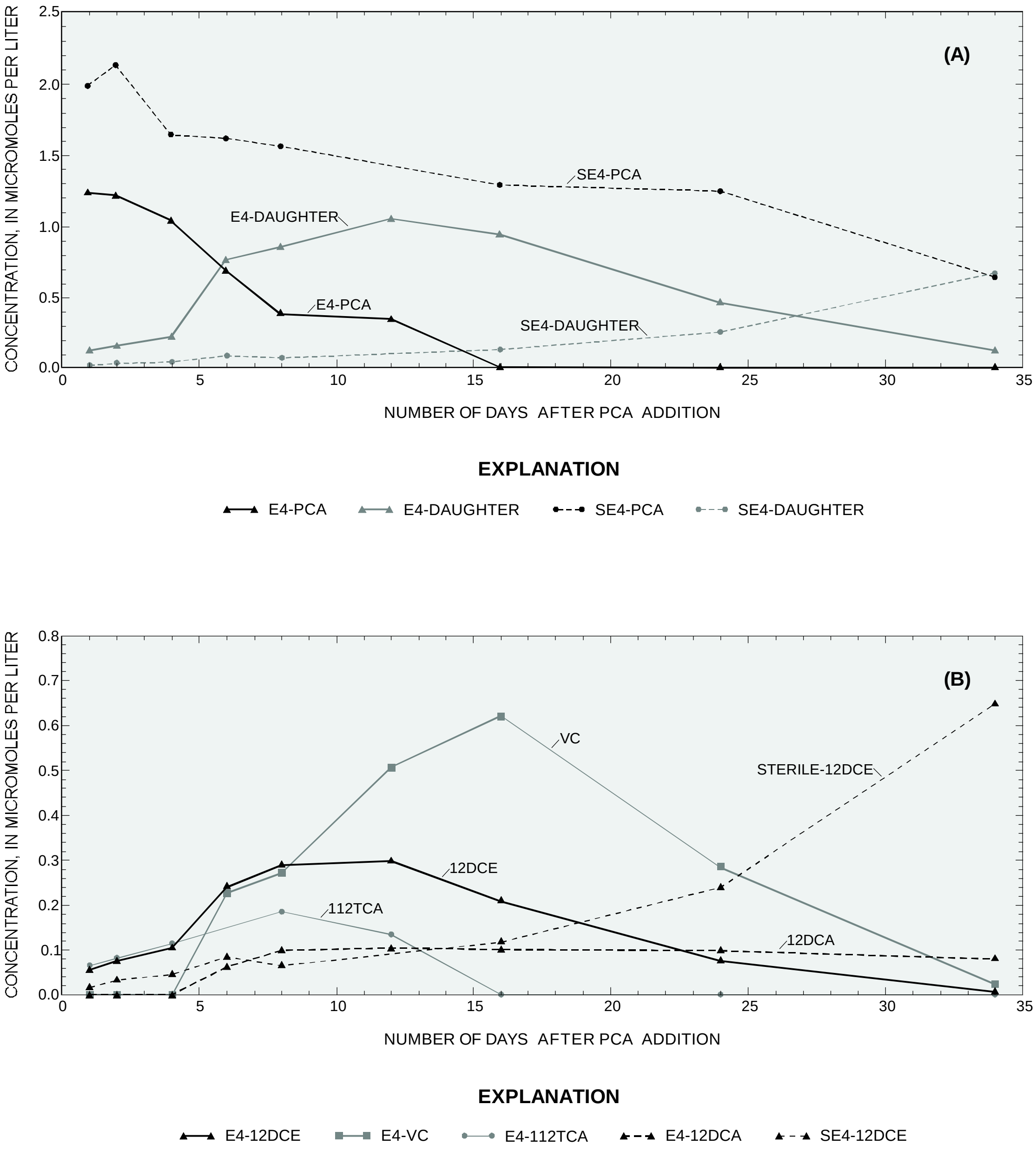


Figure 36. Degradation of 1,1,2,2-tetrachloroethane (PCA) under methanogenic conditions in microcosms amended with approximately 2.9 micromoles per liter of PCA at day 0. **(A)** Concentrations of PCA and the sum of daughter products in the non-sterile microcosms (E4) and sterile controls (SE4). **(B)** Concentrations of the daughter products, including the total of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene (12DCE), vinyl chloride (VC), 1,1,2-trichloroethane (112TCA), and 1,2-dichloroethane (12DCA).

day 0 was lost within 24 hours (table 1; figs. 34 to 36). In the methanogenic microcosms amended with TCE (experiments E2 and E3), the removal rates in the non-sterile and sterile microcosms were approximately the same during day 1 to 7, and little production of daughter products was observed during this period (figs. 34 and 35). In the microcosms amended with PCA, abiotic processes seemed to be most substantial during day 0 to 4 (table 1 and fig. 36). Sorption to the organic-rich, fine-grained wetland sediments is the most likely cause of this abiotic loss of the TCE and PCA in the microcosms. After this initial period, however, concentrations of TCE and PCA decreased rapidly in the non-sterile microcosms, while concentrations in the sterile microcosms remained approximately constant. The TCE was below detection by day 24 in the E2 and E3 microcosms, and PCA was below detection by day 16. Production of daughter compounds in the non-sterile microcosms was significant compared to the sterile microcosms, showing that biodegradation of the TCE and PCA by microorganisms indigenous to the wetland sediments was occurring.

Non-sterile microcosms amended with TCE at two concentration levels showed production of 12DCE and VC as the only daughter products (figs. 34 and 35). The sterile microcosms amended with TCE had very low concentrations of 12DCE and no detectable VC. The 12DCE, which was detected by day 4, was the first daughter product to appear, while VC appeared after day 8. These daughter products agree with the sequential degradation of TCE by hydrogenolysis (fig. 5). The total concentrations of *cis*-12DCE and *trans*-12DCE are shown in the figures. The *cis* isomer was the predominant form of the 12DCE that was produced in the TCE-amended microcosms, comprising more than 90 percent of the 12DCE in microcosm experiments E2 and E3. Hydrogenolysis of TCE has been shown to produce much higher proportions of the *cis* than the *trans* isomer of 12DCE in numerous field and laboratory studies (for example, Freedman and Gossett, 1989; de Bruin and others, 1992). Wiedemeier and others (1996, p. 2-20) state that 12DCE is likely to be a daughter product of TCE (rather than resulting from a direct contaminant release of 12DCE) if the *cis*-12DCE is greater than 80 percent of the total 12DCE.

In the E2 microcosms, the maximum concentration of the sum of the daughter products nearly equaled the concentration of TCE that was measured between day 1 to 4, indicating equimolar conversion of the TCE to 12DCE and VC (fig. 34). In the E3 microcosms, however, the maximum concentration of the sum of the daughter products was less than half of the TCE present at day 1. Although the TCE concentrations at day 1 in the E3 microcosms were more than twice as high as those in the E2 microcosms, the maximum concentration of total daughter products measured in each microcosm experiment was about 1µmol/L. Most likely, the peak concentrations of the 12DCE and VC in the E3 microcosms occurred between the sampling dates and, thus, were missed. Concentrations of the daughter products in both sets of TCE-amended microcosms decreased to below detection levels by day 34, indicating complete degradation of the vinyl chloride to carbon dioxide and water (figs. 34 and 35). Ethylene was not detected, indicating that this compound was rapidly metabolized if it was produced.

The predominant daughter products observed in the PCA-amended microcosms also were 12DCE and VC (figs. 36 and 37). The 12DCE is most likely produced through dichloroelimination of PCA (fig. 5). Although PCA could abiotically degrade to TCE, which could then degrade to 12DCE by hydrogenolysis (fig. 5), the PCA-amended microcosm results did not show any evidence of this pathway. TCE concentrations were insignificant (less than 0.05 µmol/L) throughout the experiment. Dichloroelimination of PCA to produce 12DCE was not a strictly biotic reaction because 12DCE was observed in the sterile microcosms (fig. 36). Through day 16, concentrations of 12DCE in the sterile controls were less than about 50 percent of the 12DCE measured in the non-sterile microcosms. Between day 16 and 34, the concentrations of 12DCE increased greatly in the sterile microcosms. By this time, however, all the PCA in the non-sterile-

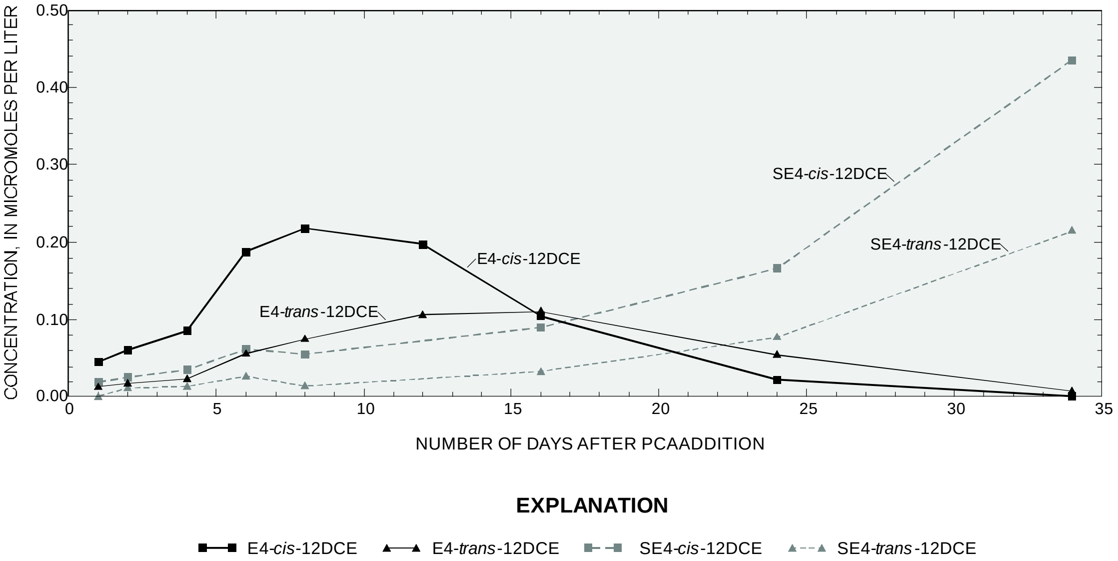


Figure 37. Concentrations of *cis*-1,2-dichloroethylene (*cis*-12DCE) and *trans*-1,2-dichloroethylene (*trans*-12DCE) produced under methanogenic conditions in non-sterile microcosms (E4) and sterile controls (SE4) amended with approximately 2.9 micromoles per liter of 1,1,2,2-tetrachloroethane (PCA) at day 0.

microcosms was degraded, and concentrations of 12DCE had reached their peak. Dichloroelimination of PCA, therefore, was enhanced in the non-sterile microcosms compared to the sterile controls. A change in some condition, such as pH, in the sterile microcosms could have made abiotic production of 12DCE more favorable after day 16, or the formaldehyde used to prepare the sterile microcosms might not have maintained effective controls. The methane concentrations remained stable around the initial concentrations in the sterile microcosms (fig. 38), but microorganisms other than methanogens could have become active.

Greater production of *trans*-12DCE was observed in the microcosms when PCA was the parent contaminant compared to TCE (fig. 37). Through day 12 in the PCA-amended microcosms, *trans*-12DCE comprised up to 25 percent of the total 12DCE, whereas it was less than 10 percent of the total 12DCE in the TCE-amended microcosms. Dichloroelimination of PCA, therefore, seemed to produce a greater proportion of the trans isomer than hydrogenolysis of TCE produced. At day 12, the concentrations of *cis*-12DCE began to decrease relatively rapidly in the PCA-amended microcosms, while the *trans*-12DCE initially stayed the same and then decreased more slowly than the *cis*-12DCE. On days 16 and 24, the *trans*-12DCE comprised about 50 and 75 percent, respectively, of the total 12DCE. The increased percentage of the *trans*-12DCE during this period probably resulted from faster degradation of the *cis*-12DCE compared to *trans*-12DCE under these anaerobic conditions. Both isomers can be biodegraded to VC by hydrogenolysis, and another microcosm study also has shown that *cis*-12DCE degradation is much faster than *trans*-12DCE (Chen and others, 1996).

These microcosm results agree with analyses of water samples that were collected from the piezometers and peepers along section C-C',

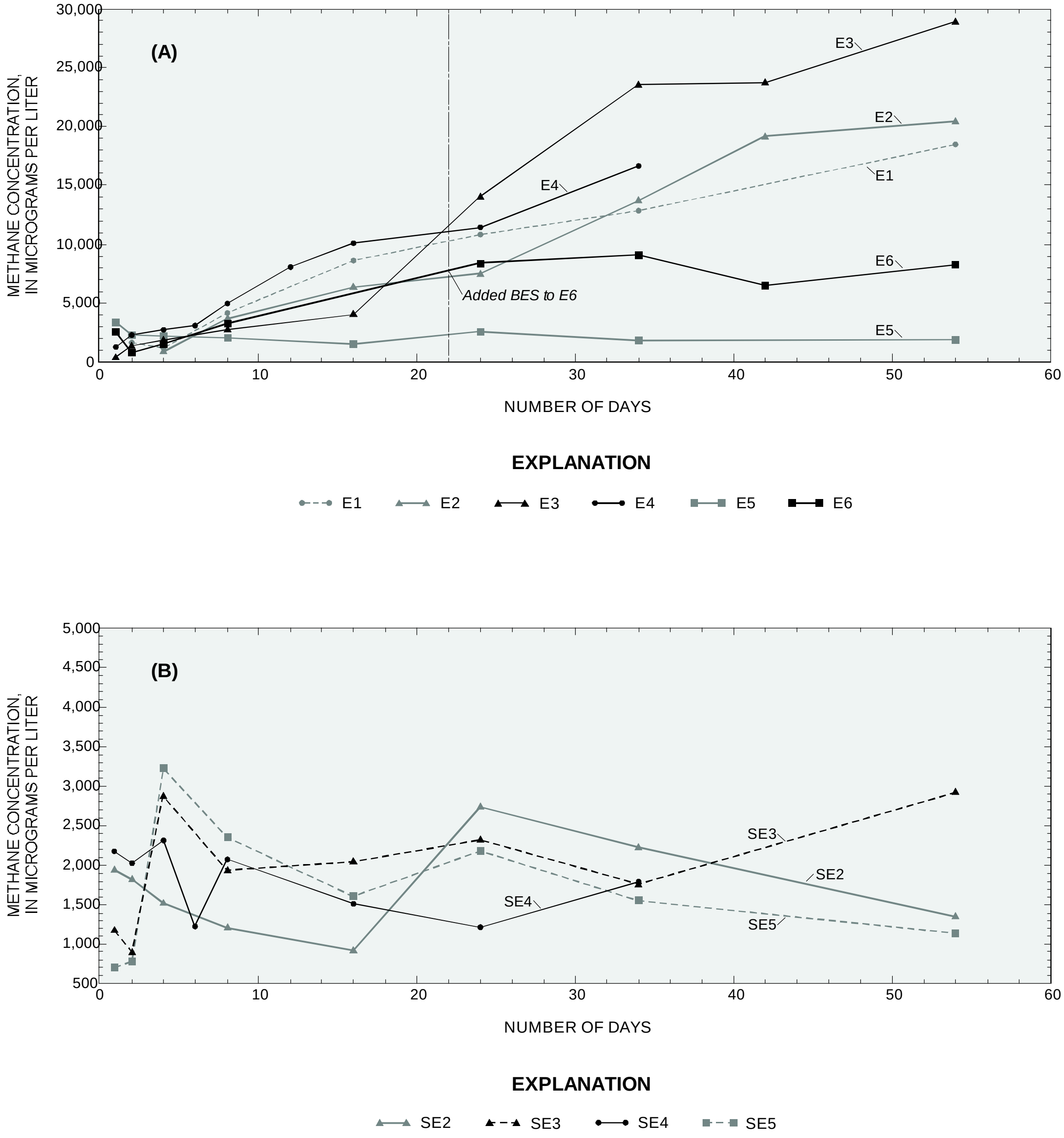


Figure 38. Concentrations of methane in anaerobic microcosms. **(A)** Non-sterile microcosms, E 1 to E6. **(B)** Sterile control microcosms, SE2 to SE5. [Refer to table 1 for the amendments to each experiment.] [*Note variation in scale.*]

where PCA was the primary parent contaminant. Here, the *trans* isomer commonly was 40 to 70 percent of the total 12DCE, indicating that the DCE isomers were affected by the relatively high amount of the *trans*-12DCE produced by dichloroelimination and by selective degradation of the *cis*-12DCE. [Concentrations of *cis*- and *trans*-12DCE in ground water are on file in the Maryland-Delaware-D.C. District office, USGS, Md.).] Along section A-A' where TCE and PCA were both parent contaminants, the *trans* isomer commonly comprised less than 30 percent of the total 12DCE in water from the wetland sediments. The relatively lower percentage of *trans*-12DCE along this section probably reflects the greater production of *cis*-12DCE by hydrogenolysis of TCE. Concentrations of 1,1-dichloroethylene were insignificant in the ground-water samples and the microcosms.

Production of 112TCA and 12DCA through hydrogenolysis reactions also was observed in the PCA-amended microcosms (fig. 36). Because VC, 112TCA, and 12DCA were not observed in the sterile microcosms amended with PCA, their production seems to be microbially mediated. The daughter products 112TCA and 12DCE were first to appear, suggesting simultaneous dichloroelimination and hydrogenolysis of PCA. Concentrations of 112TCA, however, reached their peak and then decreased to below detection levels earlier than the other daughter products. The daughter product VC reached higher concentrations and peaked later (day 16) than the other daughter products. This sequence and relative concentrations of the daughter products indicate that VC is produced by two mechanisms--dichloroelimination of the 112TCA and hydrogenolysis of the 12DCE. The sequence of appearance and the relative concentrations of the individual daughter products measured over time in the PCA-amended microcosm were very similar to those observed in ground-water samples with depth in the upward direction of flow through the wetland sediments at site WB-35, where PCA was the primary parent contaminant in the ground water (figs. 32 and 36).

The laboratory results, therefore, are consistent with field observations, confirming that 12DCE and VC are the predominant daughter products from degradation of PCA and that both dichloroelimination and hydrogenolysis pathways are important in this environment. Only one other study, conducted in the laboratory using anaerobic municipal sludge, has been found in the literature that reports evidence for both of these PCA degradation pathways under environmental conditions (Chen and others, 1996). Recognition of these PCA degradation pathways is important because they produce the same dominant daughter products as TCE degradation under anaerobic conditions. TCE and PCA are two parent contaminants that commonly occur together at Aberdeen Proving Ground and other military installations (Joseph King, U.S. Army Environmental Center, written commun., 1997). Because different proportions of *trans*- and *cis*-12DCE were produced by PCA degradation compared to TCE degradation, the isomer distribution could potentially assist in determining whether both TCE and PCA degradation are occurring at other sites on the basis of field data.

In the TCE- and PCA-amended microcosm experiments, a positive relation was observed between methane production and the production of daughter products (figs. 34 to 38), as noted from the field results. The greatest production of daughter products in the TCE-amended microcosms E2 and E3 was observed after day 8, when methane concentrations increased above 5,000 µg/L (about 312 µmol/L). Although some production of 12DCE was observed earlier in the experiments when methane concentrations were lower, vinyl chloride was not produced (figs. 35 and 36). Similarly, in the PCA-amended microcosms (E4), VC was not produced until after day 4, when methane concentrations began to rise above 5,000 µg/L. Methane production rates in microcosms E2, E3, and E4 were approximately the same as in the non-sterile control E1, which was not amended with any VOC's, especially during the period of degradation of the parent and daughter compounds (until day 34). The natural methanogenic activity in the wetland sediments, therefore, was neither inhibited or stimulated by the presence of the added contaminants. This is not surprising because the micromolar concentration range of the contaminants is much less than the natural supply of organic substrates in the wetland sediments. The amount of methane produced in association with degradation of the VOC's, therefore, would be insignificant compared to natural production rates.

The important effect of methane production on TCE biodegradation was investigated further in microcosm experiment E5, which was conducted under sulfate-reducing conditions, and in experiment E6, which included the addition of a specific inhibitor of methanogenic activity, BES (table 1). The high concentrations of sulfate added to the microcosms in E5 stimulated sulfate reduction and kept methane concentrations below about 2,500 µg/L (fig. 38). Although degradation of TCE and production of 12DCE and VC occurred under these sulfate-reducing conditions, rates were slower than observed under methanogenic conditions. At day 54, TCE was still detectable in the sulfate-reducing microcosms, and concentrations of 12DCE, and especially VC, were still increasing (fig. 39). In contrast, all the parent and daughter compounds were degraded within 34 days in the TCE- and PCA-amended microcosms under methanogenic conditions.

The microcosms in experiment E6 were constructed and treated the same as E3, except BES was added to inhibit methane production at day 22. Addition of the BES did stop the increase of methane concentrations after this time (fig. 38). The concentrations of 12DCE and VC also remained stable after addition of the BES, indicating that methanogenic activity was needed for the hydrogenolysis of 12DCE to VC and of VC to ethylene (fig. 40). The 12DCE and VC were still detectable at day 54 in the E6 microcosms, whereas these daughter products were completely degraded by day 34 in the E3 microcosms. Unfortunately, because TCE was already below detection when the BES was added, the effect of BES on the hydrogenolysis step of TCE to 12DCE could not be seen. The results of the E5 and E6 microcosms confirm other laboratory studies that have shown reductive dehalogenation of chlorinated solvents to be most rapid and complete under methanogenic conditions.

Maximum potential rates of TCE and PCA degradation were calculated from the microcosm experiments, assuming first-order degradation kinetics (table 5). Because the correlation coefficients (r^2 values) were close to or equal to 1, the assumption of first-order degradation kinetics appears to be good. The degradation rates were calculated using time periods where TCE or PCA losses in the sterile controls were less than 5 percent of the loss in the non-sterile microcosms. Degradation rate constants for TCE under methanogenic conditions (experiments E2 and E3) were 0.10 and 0.31 day^{-1}, corresponding to half-lives of 2 and 7 days. These rates are probably higher than actual field rates because the microcosms create a relatively protected, stable environment for the microorganisms. The TCE degradation rates measured for the wetland sediments are much higher than those reported in the literature for microcosms constructed with sandy aquifer sediments. For example, TCE degradation rates of 0.0001 to 0.003 day^{-1} were reported for sand aquifers at Picatinny Arsenal, New Jersey, and at a Superfund site at St. Joseph, Michigan (Rifai and others, 1995). These degradation rates are two to three orders of magnitude lower than observed in the microcosms with wetland sediments, probably because sand aquifer sediments typically have lower organic-carbon contents and microbial activity than wetland sediments. The first-order rate constant for degradation of PCA in the wetland sediments at APG was about 0.25 day^{-1}, which is close to the maximum degradation rate that was observed for TCE.

Although the degradation rate of TCE under sulfate-reducing conditions was slower than under methanogenic conditions, the rate of 0.045 day^{-1}, which gives a half-life of 15 days, is still very high. At sites where sulfate reduction was dominant in the ground water, methanogenic conditions were present in the immediate vicinity. The longer persistence of VC and 12DCE, therefore, that was observed in the microcosms under sulfate-reducing conditions should not be a problem under field conditions. Both field and laboratory results indicated rapid loss of these daughter compounds under methanogenic conditions.

In summary, the naturally anaerobic environment of the wetland sediments and the

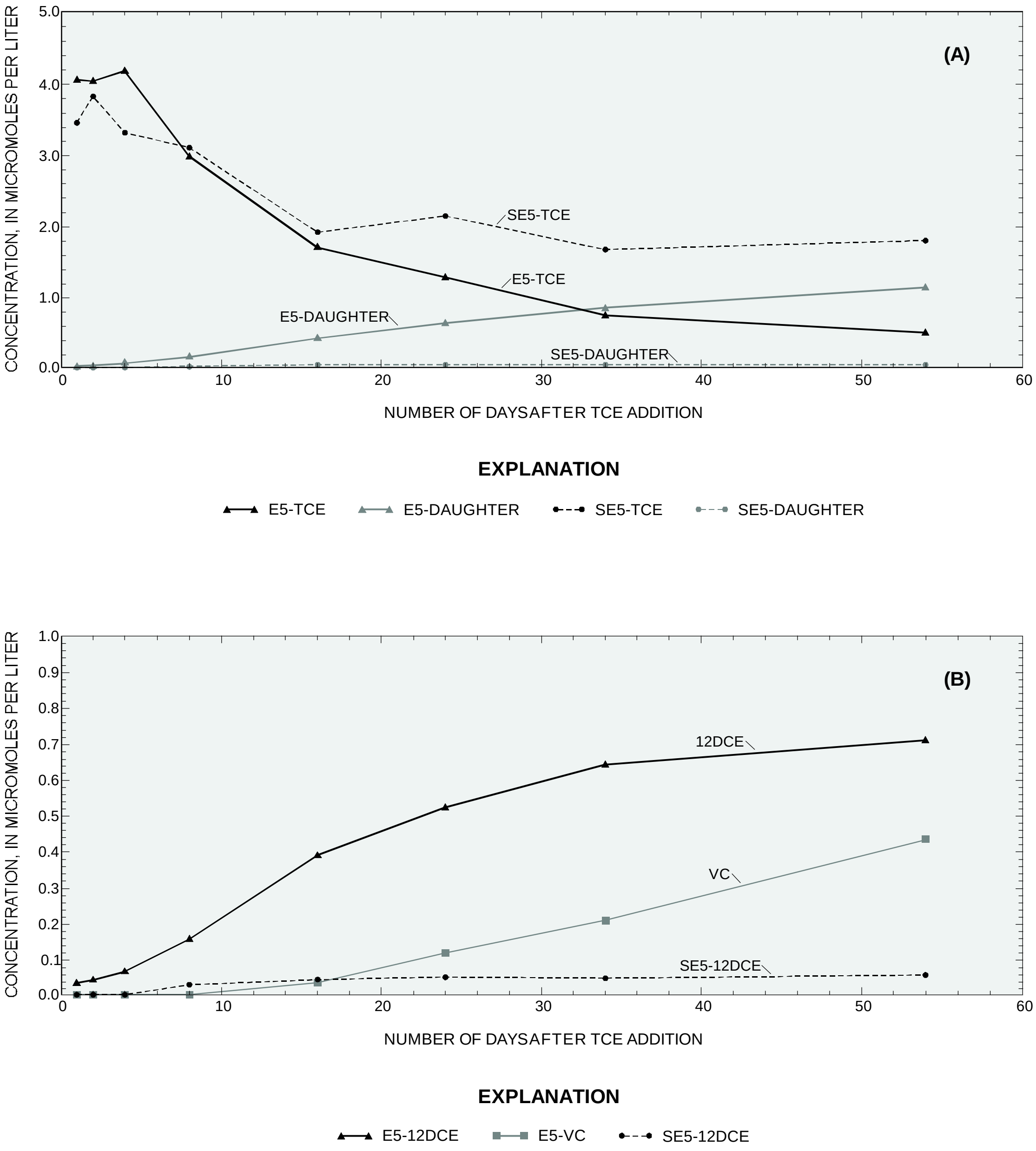


Figure 39. Degradation of trichloroethylene (TCE) under sulfate-reducing conditions in microcosms amended with approximately 7.5 micromoles per liter of TCE at day 0. **(A)** Concentrations of TCE and the sum of daughter products in the non-sterile microcosms (E5) and sterile controls (SE5). **(B)** Concentrations of the daughter products, including the total of *cis*-1,2-dichloroethylene and *trans*-1,2-dichloroethylene (12DCE) and vinyl chloride (VC).

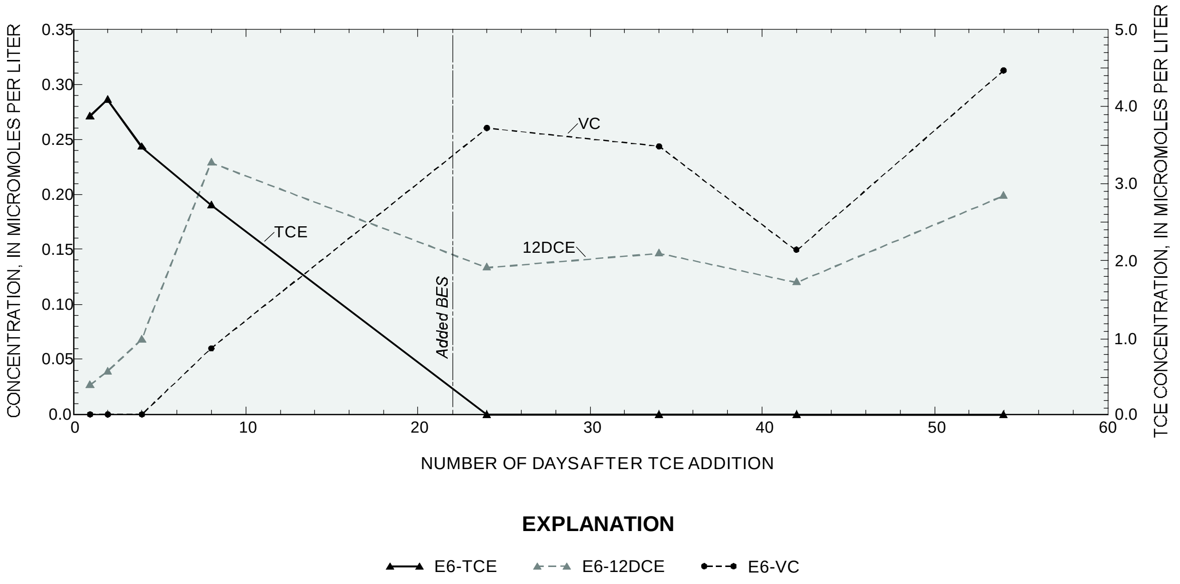


Figure 40. Degradation of trichloroethylene (TCE) in microcosms amended with approximately 7.5 micromoles per liter of TCE at day 0 and with a specific inhibitor of methanogenesis (2-bromoethanesulfonic acid, or BES) at day 22.

relatively abundant supply of natural substrates for the microorganisms probably account for the extremely high degradation rates that were observed in the microcosms. These estimated degradation rates, combined with the field evidence of the occurrence of anaerobic degradation products of TCE and PCA, indicate that natural attenuation in the wetland sediments could be an effective remediation method for the ground-water contaminants.

Aerobic Processes

Results from the microcosms that were incubated under aerobic conditions showed aerobic biodegradation of *cis*-12DCE, *trans*-12DCE, and VC. No significant removal of TCE, however, was observed in the aerobic microcosms compared to sterile controls, and these results are not shown. Figure 41 shows the decrease in concentrations of *cis*-12DCE, *trans*-12DCE, and VC in non-sterile microcosms (bnv-1) and sterile controls (bsnv-1) that were constructed with sieved sediment and amended with 1-percent methane in the headspace. Similar biodegradation rate constants were observed in the microcosms that were treated the same as bnv-1 but were constructed without sieving the sediment (brv-1 in table 6). The microcosms that contained dimethyl ether (bnv-3 and brv-3) did not show significant loss of *cis*-12DCE, trans-12DCE, and VC (fig. 41).

***Table 5**. First-order rate constants and half-lives for degradation of trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA) in the anaerobic microcosm experiments at the West Branch study area, Aberdeen Proving Ground, Maryland*

Experiment and parent compound	Rate constant (day^{-1})	Half-life (days)	Correlation coefficient (r^2)	Time period (days)
E2, TCE	0.31	2.2	1.0	8-16
E3, TCE	.10	7.0	1.0	8-16
E4, PCA	.25	2.8	.99	4- 8
E5, TCE	.045	15	.99	16-34

Initially, it was difficult establishing aerobic conditions in the microcosms. Methane concentrations increased greatly during the first 18 to 25 days of incubation for the different microcosm experiments (see fig. 42 for example), indicating anaerobic conditions. After this period, however, rapid methane consumption was observed, and methane was added to the microcosms on each sampling date after headspace withdrawal and analysis. The most rapid decrease in concentrations of *cis*-12DCE, *trans*-12DCE, and VC in experiments bnv-1 and brv-1 was observed after aerobic conditions were definitely established. Microbially mediated removal of the VOC's is indicated because concentrations did not decrease significantly in the sterile controls (fig. 41). First-order degradation rate constants were calculated for the period where aerobic conditions definitely existed (table 6). Rate constants that were calculated for the sterile controls were within the standard errors of the rate constants for the non-sterile microcosms. Abiotic loss, therefore, was not subtracted from the rates presented in table 6. No chlorinated degradation products were observed in the microcosms, as would be expected because aerobic microorganisms are known to degrade chlorinated VOC's to carbon dioxide and water through the formation of short-lived, unstable intermediates.

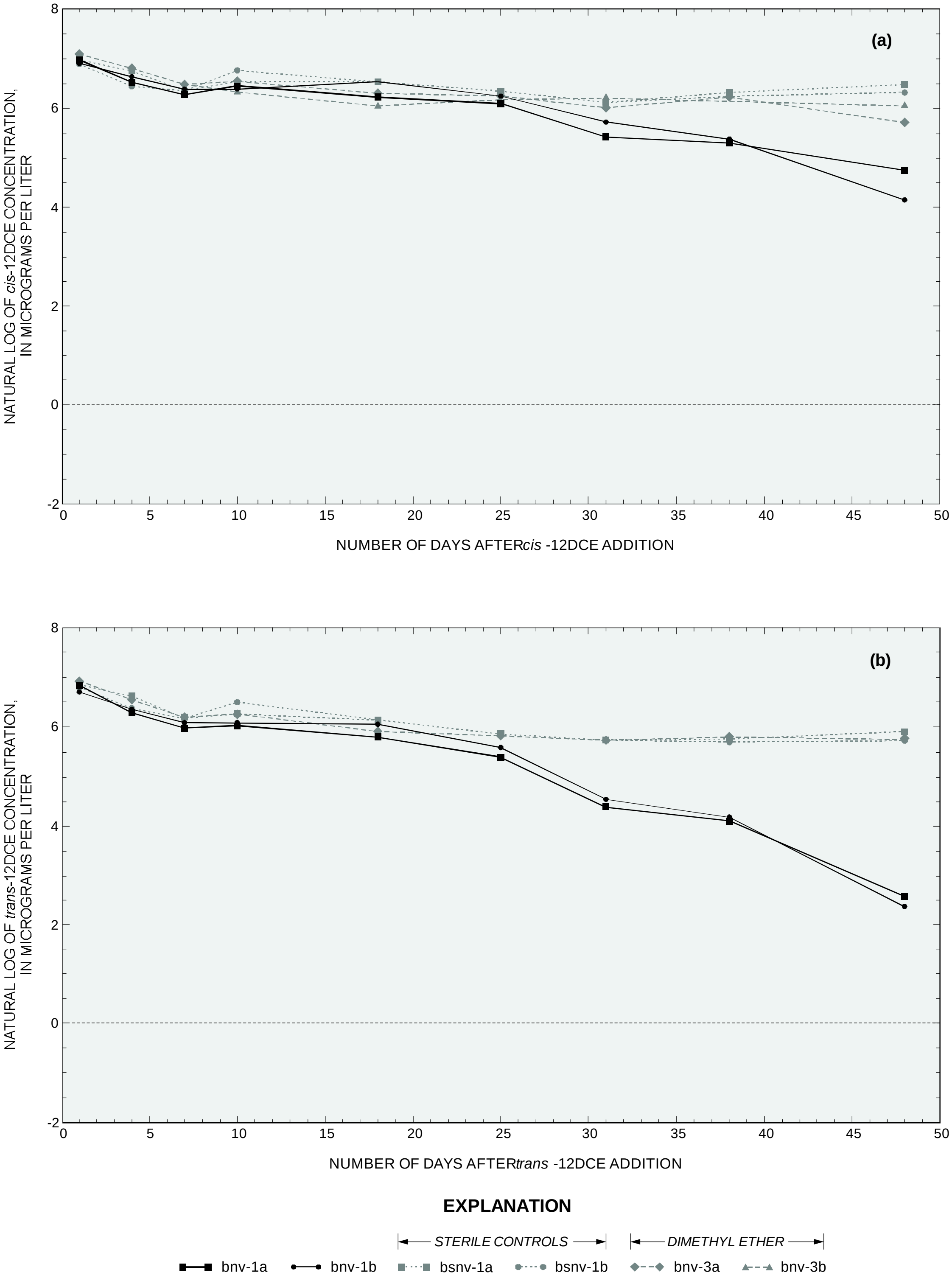


Figure 41. Aerobic degradation of **(a)** *cis*-1,2-dichloroethylene (*cis*-12DCE); **(b)** *trans*-1,2-dichloroethylene (*trans*-12DCE); and **(c)** vinyl chloride (VC) in microcosm experiments constructed with sieved sediment. [Refer to table 6 for experiment treatments.]

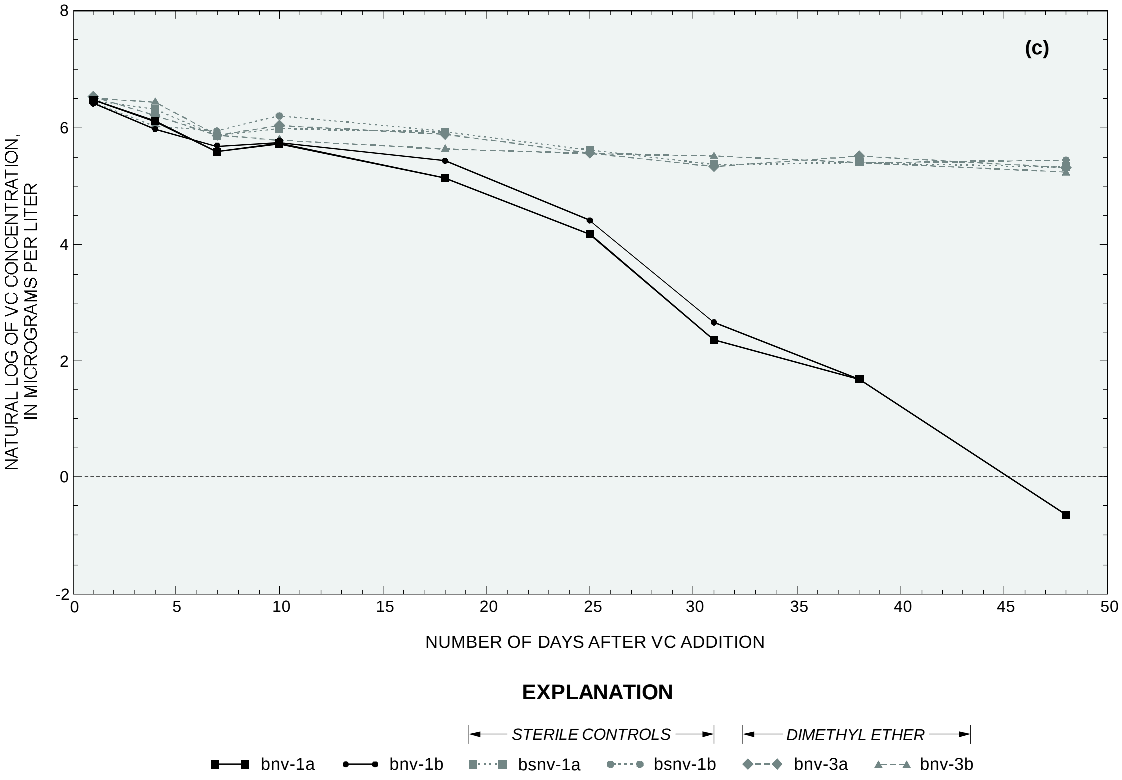


Figure 41. Aerobic degradation of **(a)** *cis*-1,2-dichloroethylene (*cis*-12DCE); **(b)** *trans*-1,2-dichloroethylene (*trans*-12DCE); and **(c)** vinyl chloride (VC) in microcosm experiments constructed with sieved sediment. [Refer to table 6 for experiment treatments.] -- Continued.

Table 6. *First-order rate constants and half-lives for degradation of cis-1,2-dichloroethylene (cis-12DCE), trans-1,2-dichloroethylene (trans-12DCE), and vinyl chloride (VC) in the aerobic microcosm experiments at the West Branch study area, Aberdeen Proving Ground, Maryland*

[Rate constants are presented for duplicate microcosms for each experiment, and the standard error is given for a 95-percent confidence interval after the plus or minus (±)]

Experiment	Rate constant (day^{-1})	Half-life (days)	Correlation coefficient (r^2)	Time period (days)
cis-**12DCE:**				
brv-1	0.06 ± 0.01	12	0.88	18-48
	.05 ± .01	14	.84	18-48
bnv-1	.05 ± .01	14	.93	25-48
	.09 ± .01	7.7	.97	25-48
trans-**12DCE:**				
brv-1	.11 ± .02	6.3	.90	18-48
	.09 ± .005	7.7	.99	18-48
bnv-1	.12 ± .02	5.8	.96	25-48
	.13 ± .02	5.3	.97	25-48
VC:				
brv-1	.20 ± .04	3.4	.88	18-48
	.19 ± .02	3.6	.96	18-48
bnv-1	.20 ± .02	3.4	.97	25-48
	.21 ± .02	3.3	.99	25-48

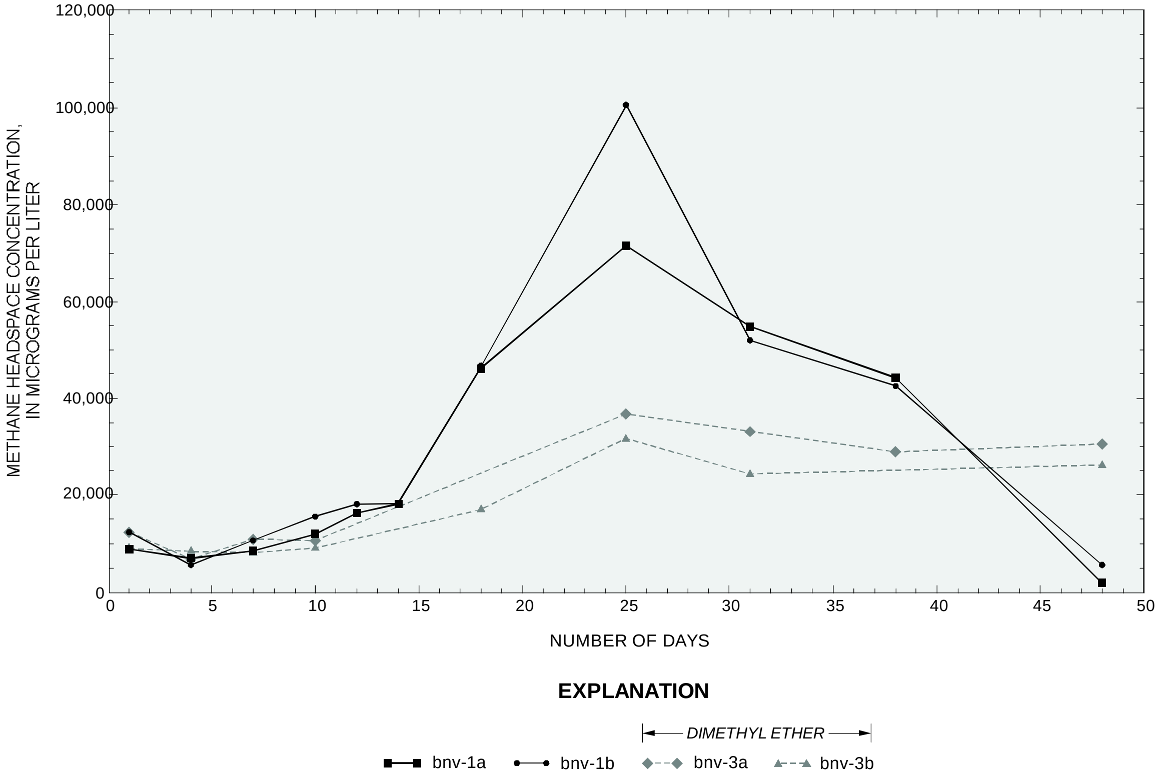


Figure 42. Methane consumption in aerobic microcosm experiments amended with *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, and vinyl chloride and constructed with sieved sediment. [Refer to table 6 for experiment treatments.]

Methane consumption was not observed in the microcosms amended with dimethyl ether, showing that methanotrophic activity was inhibited (fig. 42). Because concentrations of *cis*-12DCE, *trans*-12DCE, and VC remained the same in the microcosms amended with dimethyl ether compared to sterile controls (fig. 41), biodegradation of these compounds did seem to require the activity of methanotrophs. Biodegradation rates were the same in the microcosms constructed with sieved sediment and unsieved sediment, indicating that the presence of root material did not affect methanotrophic activity. Methanotrophs in the wetland sediments, therefore, seem to be distributed throughout the soil and not necessarily associated with roots.

Aerobic biodegradation in the microcosms was fastest for VC and lowest for *cis*-12DCE (not including the undetectable TCE degradation) (table 6). These results agree with other laboratory studies that have shown faster degradation by methane-utilizing cultures when the compounds are less halogenated. A field experiment, in which oxygen and methane were injected into an aquifer to stimulate aerobic biodegradation, also showed that degradation of VC is more rapid than degradation of dichloroethylene compounds and that degradation of *trans*-12DCE is faster than degradation of *cis*-12DCE (Semprini and others, 1990).

The rate constants for aerobic biodegradation of *cis*-12DCE, *trans*-12DCE, and VC were as high as those measured for TCE and PCA under anaerobic conditions (tables 5 and 6). Thus, production of these daughter compounds by anaerobic biodegradation of TCE and PCA could be balanced by their consumption where oxygen is available in the wetland sediment, such as at the sediment-water interface and near plant roots. Aerobic biodegradation could, at least partially, account for the loss of these daughter products that was observed in the ground water near the surface of the wetland (for example, fig. 32). Although field evidence of the occurrence of aerobic degradation is not available, field observations of the extensive root system during drilling in the wetland sediments, in conjunction with the laboratory evidence of methanotrophic activity presented here, suggest that aerobic degradation of the less-chlorinated VOC's could be a significant process.

Sorption

To estimate K_d's in the wetland sediments, short-term (24-hour) equilibrium isotherms were measured in batch tests for the parent compound PCA and the predominant daughter contaminants (figs. 43 to 46). Results from the methanogenic microcosms indicated significant abiotic losses of TCE and PCA during the first 4 to 7 days of the experiments. More than about 85 percent of the total abiotic loss of TCE and PCA during this initial 7-day period occurred during the first day. On the basis of these results, it was assumed that short-term equilibrium could be established within 24 hours for the batch sorption tests. Longer batch tests would have required the addition of an inhibitor of microbial activity, which could affect the amount of sorption. Isotherms were measured over a wider range of concentrations for PCA than for *cis*-12DCE, *trans*-12DCE, and VC in the batch tests, because the field data showed that the parent compound was present in the ground water in higher concentrations than the daughter compounds. Sorption isotherms were not obtained for TCE, the other major parent contaminant, but abiotic losses in the anaerobic microcosms indicated that the K_d for TCE would be approximately the same as for PCA.

The equilibrium isotherms indicate that sorption to the wetland sediment is a substantial attenuation mechanism for PCA, *cis*-12DCE, and *trans*-12DCE, whereas sorption of VC is relatively lower. The estimated K_d's for PCA, *cis*-12DCE, *trans*-12DCE, and VC are about 2.3, 1.8, 2.4, and 1.3 L/kg, respectively. Sorbed concentrations of PCA, *cis*-12DCE, and *trans*-12DCE in the wetland sediments, therefore, would be expected to be about twice the concentration measured in the water, whereas sorbed concentrations of VC would not be much greater than the aqueous concentrations. On the basis of the correlation coefficients (r^2 values), the assumption of linearity provided a good fit for the data for PCA, *cis*-12DCE, and VC. The r^2 of 0.70 for *trans*-12DCE is not as good, however, and is probably due to a greater degree of difference between the duplicate batch tests for *trans*-12DCE than measured for the other compounds. The fact that the sorption isotherm for PCA maintained linearity over the full range of aqueous concentration, which covered 5 orders of magnitude, is not surprising because the maximum aqueous concentration that was added to the batch test was much less than half of the solubility of PCA. The number of sorption sites can be assumed to be large compared to the contaminant concentration, if aqueous concentrations are less than half of the compound's solubility (Lyman, 1982). In addition, linearity over high concentration ranges can be indicative of a sorption mechanism of partitioning into organic matter (Chiou and others, 1983).

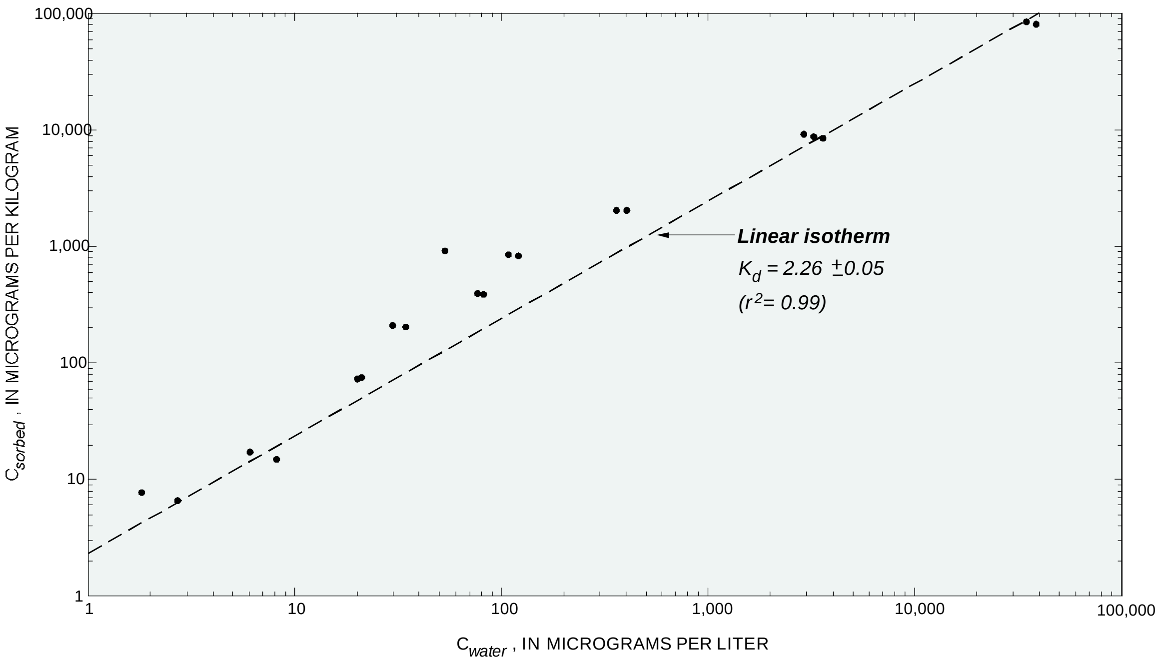


Figure 43. Sorbed (C_{sorbed}) and aqueous (C_{water}) concentrations of 1,1,2,2-tetrachloroethane (PCA) measured in 24-hour batch experiments.

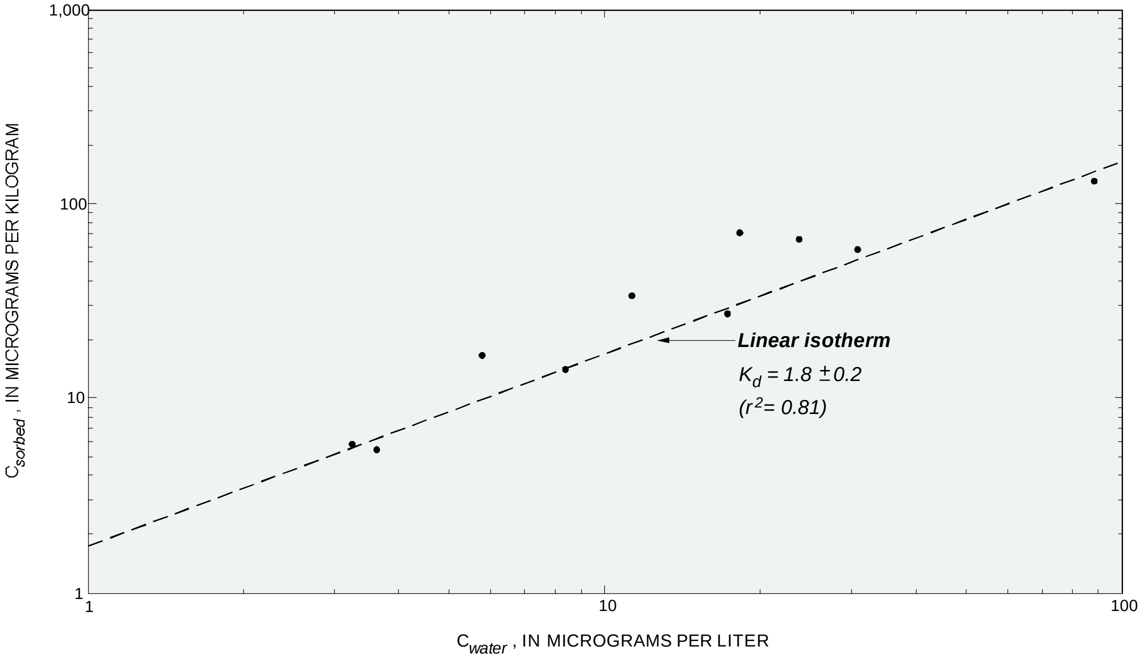


Figure 44. Sorbed (C_{sorbed}) and aqueous (C_{water}) concentrations of *cis* -1,2-dichloroethylene (*cis*-12DCE) measured in 24-hour batch experiments.

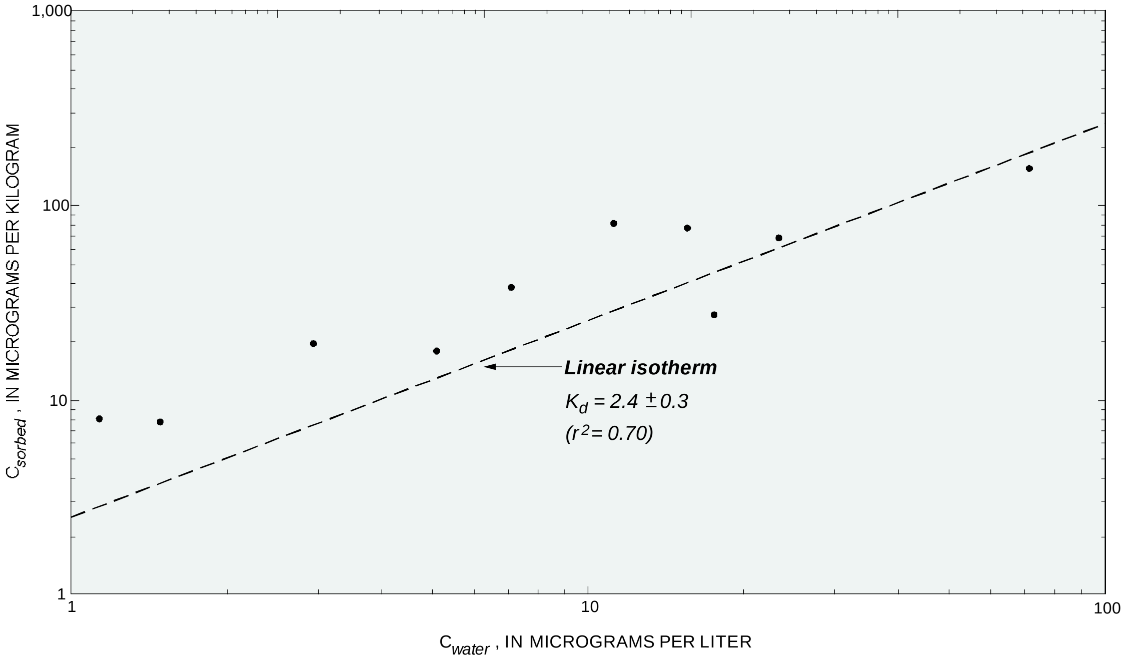


Figure 45. Sorbed (C_{sorbed}) and aqueous (C_{water}) concentrations of *trans* -1,2-dichloroethylene (*trans*-12DCE) measured in 24-hour batch experiments.

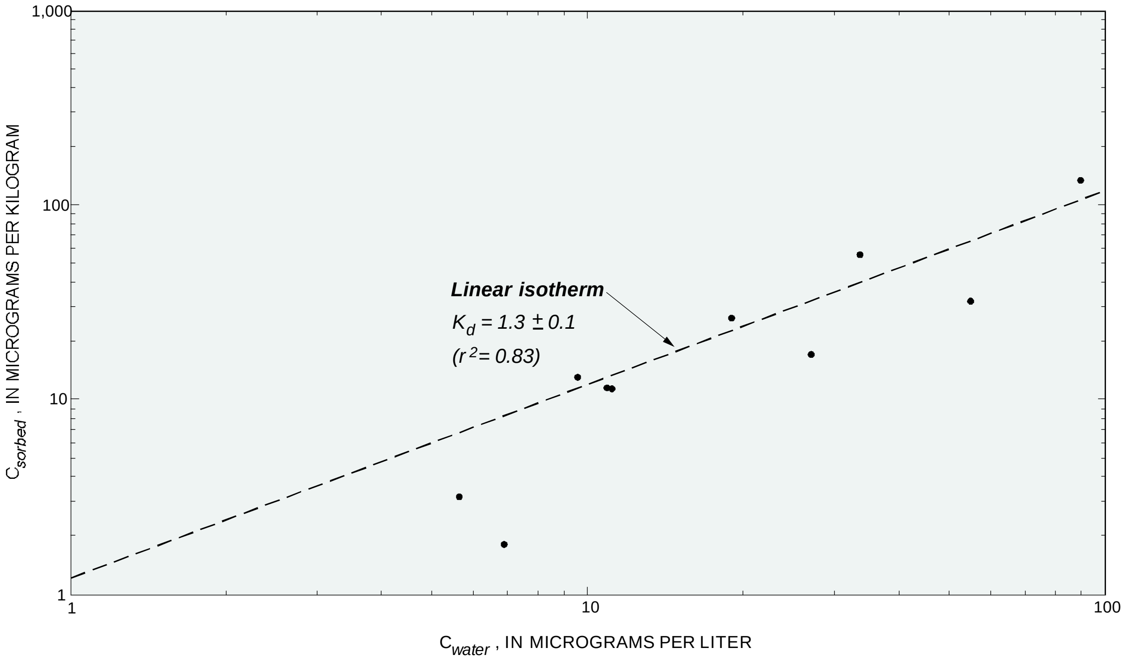


Figure 46. Sorbed (C_{sorbed}) and aqueous (C_{water}) concentrations of vinyl chloride (VC) measured in 24-hour batch experiments.

The estimated K_d's might seem relatively low on the basis of the high total organic-carbon content measured in the upper peat unit of the wetland sediments. Sorption, however, is predominately controlled by small particles with large surface areas (Schwarzenbach and Westall, 1981), and much of the organic carbon measured in the upper peat unit was probably large pieces of undecomposed or partially decomposed roots and plant debris. The total organic-carbon content of 15 samples that were collected from the upper peat unit averaged 18 percent, while total organic-carbon content averaged about 1 percent in four sediment samples that were collected from the lower clayey unit of the wetland sediment (Olsen and others, 1997). The batch sorption tests were conducted using a mixture of sediment from the two wetland sediment units that was sieved to remove large pieces of organic matter (greater than 0.187 in.). The organic-carbon content of the sediment that was used in the batch sorption tests, therefore, might have been similar to the total organic-carbon content of the lower clayey unit (about 1 percent). This is supported by comparison of the estimated K_d's to K_d's calculated from K_{oc} values (sorption coefficients normalized for organic-carbon content) reported in the literature. The empirical relation between K_d and K_{oc} is

$$K_d = (K_{oc})(f_{oc}) \quad , \qquad (10)$$

where

f_{oc} is the fraction of organic carbon in the sediment (Roy and Griffin, 1985).

For example, the K_{oc} of PCA has been estimated as 117 (Montgomery and Welkom, 1990, p. 491). The calculated K_d for PCA would equal the K_d determined from the batch tests (2.3), if the f_{oc} was 0.02 (2 percent), which is within the range of organic-carbon contents measured for the lower wetland sediment unit. If the fraction of organic carbon sorbing the PCA was as high as 18 percent, the calculated K_d for PCA would be 21. In contrast, a median f_{oc} of 0.000026 was measured from 32 sediment samples from the Canal Creek aquifer (Lorah and Vroblesky, 1989, p. 83), indicating that sorption of the VOC's would be minimal in the aquifer.

The batch sorption tests with the wetland sediment gave a general order of strongest sorption of PCA and *trans*-12DCE, followed by *cis*-12DCE, and then VC. This order is consistent with the more hydrophobic nature of PCA, as shown by a higher octanol-water partitioning coefficient (K_{ow}), compared to *cis*-12DCE and VC (Lorah and Vroblesky, 1989, p. 79). Another study that measured retardation factors in laboratory batch tests and field tracer tests also found higher sorption of *trans*-12DCE than *cis*-12DCE in sandy aquifer sediments (Roberts and others, 1990). The approximately equal K_d's estimated for PCA and *trans*-12DCE in the current study was unexpected, but the low r^2 value for the sorption isotherm for *trans*-12DCE must be considered when comparing the K_d's.

The estimated K_d from the sorption experiments can be used to calculate coefficients of retardation for each compound, which would indicate the degree that sorption retards the transport of the contaminant compared to the advective ground-water velocity. The coefficient of retardation, R, is calculated from

$$R = 1 + (P_b K_b)/n \quad , \qquad (11)$$

where

P_b is the bulk mass density [$P_b = P_s$ (1-n) where P_s is the particle mass density];

K_d is the distribution coefficient; and n is porosity.

If a particle mass density of 2.65 g/cm^3 and porosity of 0.4 is assumed for the wetland sediment, P_b is 1.59 g/cm^3. Using the average linear velocity of about 2 ft/yr that was estimated for advective flow in the wetland sediments, the coefficient of retardation for PCA, *cis*-12DCE, *trans*-12DCE, and VC, respectively, would be about 10, 8, 10, and 6. This indicates that sorption alone would cause the movement of the contaminants to be 6 to 10 times slower than the movement by advective ground-water flow through the wetland sediments.

Sorbed concentrations of VOC's were measured on 29 sediment samples that were collected during installation of the final monitoring network. Most of these sediment samples (26) were collected from the upper and lower units of the wetland sediments. Relatively high concentrations of sorbed VOC's were found in only five of these samples (table 7), although later ground-water analyses showed that contamination existed at all of the sites. At all the other sites, concentrations of the VOC's were close to or below the reporting limit of 30 µg/kg of dry soil. The low number of sediment samples that contained detectable concentrations of VOC's could be due to the relatively low number of samples collected, the small sample sizes that were extracted for VOC's, and the heterogeneous nature of the flow system. It also is possible that sorption is most significant where the contaminants first enter the lower wetland sediments and the less reducing conditions limit the rate of biodegradation.

TCE, *trans*-12DCE, and *cis*-12DCE were detected in the five samples, although concentrations of *trans*-12DCE and *cis*-12DCE were sometimes estimated because the peaks were below the detection limit (table 7). PCA and 112TCA also were detected in one sample, and tetrachloroethylene (PCE) was detected in several samples. The maximum sorbed concentrations of PCA, TCE, *trans*-12DCE, and *cis*-12DCE, respectively, were 2,500, 680, 280, and 210 µg/kg of dry soil. The maximum concentrations of PCA and *trans*-12DCE, in addition to the one detection of 112TCA, were measured in a sediment sample collected from the upper peat unit at site WB-35, which is the only site that had high concentrations of PCA in ground water in the wetland sediment. The sediment sample at site WB-35 that contained sorbed PCA was collected at a depth of 1.5 ft, whereas pore-water samples from the peepers did not show detectable PCA between 0 and 2 ft below land surface (fig. 32). Similarly, the maximum sorbed concentration of

Table 7*. Sorbed concentrations of volatile organic compounds detected in sediment samples that were collected during installation of final monitoring network in the West Branch study area, Aberdeen Proving Ground, Maryland*

[All concentrations in micrograms per kilogram of dry soil. Sample number gives the piezometer and sediment-core site number, followed by (after the dash) the sample depth, in feet below land surface; and "R" in front of the site number indicates a laboratory duplicate extraction and analysis of the sample; t, trace amount detected; E, value detected below the reporting limit and given as an estimated value; <, less than]

Sample no.	Sampling date	1,1,2,2-Tetrachloro-ethane	1,1,2-Trichloro-ethane	Tetrachloro-ethylene	Trichloro-ethylene	1,2-*trans*-Dichloro-ethylene	1,2-*cis*-Dichloro-ethylene
WB21-2.5	07-12-1994	<30	<30	t	130	E11	E23
R-WB21-2.5	07-12-1994	<30	<30	t	130	E12	E22
WB22-5	07-13-1994	<30	<30	E9.5	580	E19	210
R-WB22-5	07-13-1994	<30	<30	E12	680	E21	160
WB27-3	07-20-1994	<30	<30	122	51	E10	E21
WB35-1.5	07-22-1994	2,500	72	88	370	280	110
WB36-4	07-21-1994	<30	<30	<30	93	230	63

TCE was measured in a sediment sample collected from a depth of 5 ft at site WB-22, but water samples from the wetland sediment unit at depths of 1.5 and 7.0 ft below land surface had TCE concentrations of less than 0.2 and 70 μg/L, respectively (fig. 17). Therefore, although desorption of the sorbed contaminants is most likely occurring, biodegradation or other attenuation mechanisms seem to remove the compounds from the water at a faster rate than the desorption rate. This comparison assumes that the concentrations measured in water samples in the summer of 1995 are indicative of aqueous concentrations in the summer of 1994, when the sediment samples were collected. Because ground-water concentrations remained approximately stable throughout 1996, this assumption seems reasonable.

SUMMARY AND CONCLUSIONS

Plumes of contaminated ground water that are flowing toward or currently discharging to wetland areas present unique remediation problems because of the hydrologic connections between ground water and surface water and the sensitive ecosystem in wetlands. Natural attenuation is a promising *in-situ* treatment method for chlorinated volatile organic compounds (VOC's) that would leave the ecosystem largely undisturbed and be cost effective. Wetlands are ideal environments for natural attenuation of organic contaminants because the sediments typically have a large diversity of microorganisms and redox conditions that could enhance biodegradation and a large amount of natural organic material to sorb contaminants and provide substrates for microorganisms. During 1992-97, the U.S. Geological Survey (USGS) investigated the natural attenuation of chlorinated VOC's in a contaminant plume that discharges from a sand aquifer to a freshwater tidal wetland along the West Branch Canal Creek at Aberdeen Proving Ground, Maryland. Characterization of the hydrogeology and geochemistry along flowpaths in the wetland and determination of the occurrence and rates of biodegradation and sorption show that natural attenuation could be a feasible remediation method for the contaminant plume that extends along the West Branch Canal Creek.

The Canal Creek aquifer, which received contaminants in the past from sources that were located upgradient of the current eastern boundary of the wetland, is 40 to 45 ft thick in the study area. The overlying wetland sediments consist of two distinct layers that have a combined thickness of 6 to 12 ft--an upper unit of peat and a lower unit of silty to sandy clay or clayey sand. Head distributions show strong vertical gradients, and flow directions are predominantly upward through the wetland sediments. Tidal fluctuations, however, cause some reversals in flow directions and changes in discharge locations, which affect the distribution and transport of contaminants. The reversals in flow and downward infiltration of surface water can increase the effects of dispersion and can prolong residence times of contaminants in the wetland sediments, which would allow more time for attenuation reactions such as biodegradation to occur. The average linear velocity of ground water is estimated to be about 2 to 3 ft/yr along vertical flow lines in the wetland area, and the total ground-water discharge along a 1-ft-wide strip of the wetland extending from the eastern wetland boundary to the creek is in the range of 0.13 and 0.25 ft^2/d. Flow velocities could be more than an order of magnitude higher, however, if water flows through preferential flowpaths, such as breaches in clay layers in the aquifer or root channels in the wetland sediments.

The major parent contaminants in the aquifer were trichloroethylene (TCE); 1,1,2,2-tetrachloroethane (PCA); carbon tetrachloride (CT); and chloroform (CF). The aquifer was typically aerobic (dissolved oxygen concentrations greater than 1 mg/L), but ground water in the wetland sediments became increasingly anaerobic along the upward flow direction. Iron-reducing conditions were predominant in the lower wetland sediment unit composed of clayey sand and silt, and methanogenesis was predominant in the upper unit composed of peat. Although sulfate-reducing conditions were dominant only in a few localized zones, low concentrations of sulfide were more commonly found in conjunction with methane. Comparisons with water samples collected at the background site show that anaerobic conditions exist naturally in the wetland sediments. The wetland sediments, therefore, show favorable conditions for natural attenuation of chlorinated VOC's, because biodegradation of highly chlorinated VOC's, such as TCE and PCA, can occur most easily under anaerobic conditions and is believed to be fastest under the highly reducing conditions of methanogenesis.

Field and laboratory evidence indicate that anaerobic degradation of TCE and PCA does occur in the wetland sediments. Total concentrations of VOC's and the relative proportions of parent compounds to anaerobic daughter products changed substantially as the contaminants were transported upward through the changing redox environments. Concentrations of the parent compounds TCE and PCA ranged from about 100 to 2,000 µg/L in the aquifer beneath the wetland, whereas concentrations of daughter products were low or undetectable. In contrast, the parent compounds commonly were not detected in ground water in the wetland sediments, but the daughter compounds 1,2-dichloroethylene (12DCE), vinyl chloride (VC), 1,1,2-trichloroethane (112TCA), and 1,2-dichloroethane (12DCA) were observed. 12DCE and VC were the dominant daughter products in the wetland sediments, even where PCA was the primary parent contaminant discharging to the wetland. The presence of these daughter products in water in the wetland sediments indicates that TCE is degraded by hydrogenolysis reactions and that PCA is degraded by the two reductive dechlorination pathways of hydrogenolysis and dichloroelimination. Concentrations of 12DCE were typically higher than VC in the lower wetland sediment unit, whereas concentrations of VC increased in the upper peat unit where methane concentrations increased.

Total concentrations of VOC's, however, decreased upward through the 6- to 12-ft-thick wetland sediments and were less than 5 µg/L near the surface. The daughter products are apparently further degraded by these anaerobic processes to non-chlorinated, nontoxic end products, or are removed by other attenuation processes such as aerobic degradation or volatilization. The parent contaminants CT and CF also are most likely degraded through anaerobic hydrogenolysis reactions in the wetland sediments. Concentrations of these compounds typically were below detection throughout the wetland sediments.

Several sets of anaerobic microcosms, some amended with TCE concentrations of 400 or 990 µg/L (3.0 or 7.5µmol/L) and one amended with a PCA concentration of 480 µg/L (2.9 µmol/L), were constructed in the laboratory using wetland sediment and ground water from the study area. These microcosm experiments confirmed field observations that 12DCE and VC are the dominant daughter products from anaerobic biodegradation of both TCE and PCA. Production of 112TCA and 12DCA also was observed in the PCA-amended microcosms, but concentrations were lower than those of 12DCE and VC. Because 112TCA and 12DCE were the first daughter products to appear in these microcosms, PCA degradation by hydrogenolysis and dichloroelimination seems to occur simultaneously. Daughter products were not observed in sterile controls, except for relatively low concentrations of 12DCE in the PCA-amended controls. Parent and daughter concentrations in the non-sterile microcosms decreased to less than 5 µg/L in less than 34 days under methanogenic conditions, thus showing extremely rapid biodegradation rates in these organic-rich wetland sediments.

Maximum potential rate constants for biodegradation of TCE and PCA, which were calculated from the microcosm experiments assuming first-order degradation kinetics, ranged from 0.10 to 0.31 day^{-1} under methanogenic conditions, corresponding to half-lives of 2 to 7 days. These estimated rate constants for the wetland sediments are two to three orders of magnitude higher than those reported in the literature for TCE biodegradation in microcosms constructed with sandy aquifer sediments. Microcosms that were constructed with wetland sediment under sulfate-reducing conditions in the present study had slower rates of biodegradation compared to the wetland sediment under methanogenic conditions, but still had faster rates than those reported for sand aquifer sediments. The maximum rate constant under sulfate-reducing conditions was 0.045 day^{-1}, which gives a half-life of 15 days.

Aerobic biodegradation rates for *cis*-12DCE, *trans*-12DCE, and VC were as high as those measured for TCE and PCA under anaerobic conditions in microcosm experiments. Thus, production of these daughter products by anaerobic biodegradation of TCE and PCA could be balanced by their consumption where oxygen is available in the wetland sediment, such as near plant roots and land surface. Aerobic biodegradation of *cis*-12DCE, *trans*-12DCE, and VC in the microcosms coincided with periods of methane consumption, and biodegradation was not observed in microcosms that were amended with the inhibitor dimethyl ether. These results indicate that biodegradation of *cis*-12DCE, *trans*-12DCE, and VC under aerobic conditions required the activity of methanotrophs. Aerobic biodegradation was fastest for VC and slowest for TCE. These results agree with other laboratory and field studies that have shown faster degradation by methane-utilizing cultures when the compounds are less halogenated. Although field evidence of the occurrence of aerobic degradation is not available, field observations during drilling of the extensive root system in the wetland sediments, in conjunction with the laboratory evidence of methanotrophic activity, suggest that aerobic degradation of the less-chlorinated VOC's could be a significant process.

Sorption also is a significant natural attenuation process in the wetland sediments. Equilibrium sorption isotherms were measured in 24-hour batch tests and used to estimate distribution coefficients (K_d's) to describe the ratios of sorbed to aqueous concentrations of PCA and the daughter products *cis*-12DCE, *trans*-12DCE, and VC. The estimated K_d's for PCA, *cis*-12DCE, *trans*-12DCE, and VC were about 2.3, 1.8, 2.4, and 1.3 L/kg, respectively. Sorbed concentrations of PCA, *cis*-12DCE, and *trans*-12DCE in the wetland sediments, therefore, would be expected to be about twice the concentration measured in the water, whereas sorbed concentrations of VC would not be much greater than the aqueous concentrations. These K_d's are consistent with the more hydrophobic nature of PCA, as shown by a higher octanol-water partitioning coefficient, compared to *cis*-12DCE and VC. The approximately equal K_d's estimated for PCA and *trans*-12DCE in the current study was unexpected, but the assumption of linearity made to calculate the K_d's did not provide as good of a fit to the data for *trans*-12DCE as the other compounds. Coefficients of retardation, which were calculated using the K_d's and an advective flow velocity of about 2 ft/yr, indicate that sorption alone would cause the movement of the contaminants through the wetland sediments to be 6 to 10 times slower than the advective ground-water flow.

In addition to the laboratory measurements, sorbed concentrations of VOC's were measured on 26 sediment samples that were collected at contaminated sites from the upper and lower units of the wetland sediments. Significant concentrations of sorbed VOC's were found in only five of these samples. The low number of sediment samples that contained detectable concentrations of VOC's could be due to the relatively low number of samples collected and the heterogeneous nature of the flow system. It also is possible that sorption is most significant where the contaminants first enter the lower wetland sediments and the less reducing conditions limit the rate of biodegradation.

In conclusion, biodegradation is an important natural attenuation mechanism in the wetland sediments for chlorinated hydrocarbons, as shown by the reduction in concentrations of the parent VOC's, the production of daughter compounds, and the extremely rapid degradation rates measured in laboratory experiments. Laboratory measurements indicated that sorption to the organic-rich, fine-grained wetland sediments could also retard movement of the contaminants. The relatively thin layers of wetland sediments, therefore, are critical in reducing contaminant concentrations and toxicity of the ground water before it discharges to the wetland surface and the creek. Natural attenuation in the wetland sediments could be an effective remediation method for the ground-water contaminants.

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